The High-frequency Conductivity of Aqueous Solutions of Colloidal Electrolytes.

by

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Contents.

INTRODUCTION.

Certain substances, in sufficiently dilute aqueous solution, behave as simple strong electrolytes but, at higher concentrations, exhibit properties which can be explained only on the basis of aggregation of the constituent ions. Often, the transition from the simple behaviour to the complex, is extremely sharp, occurring at a so-called "critical concentration." This concentration depends on the size, shape and charge of the aggregating ions.[1] While, as a rule, substances exhibiting this behaviour are salts containing long chains of carbon atoms, this is not a necessary criterion. As a class, these substances are assigned the name of "colloidal electrolytes," a term descriptive of their dual nature.

Investigators of the properties of solutions of these substances are in unanimous agreement on the existence of aggregation. Regarding the shape, size and size distribution (if any) of these aggregates there are the most diverse views.

Until recently, McBain, one of the foremost workers in this field, postulated two types of micelle, a small spherical, highly conducting "ionic micelle" and a larger, lamellar, poorly conducting "neutral micelle," the relative proportions of which varied with concentration. Now, however, McBain appears to have

abandoned this view and, while relying on two types as before, assigns to these different resulting charges and varying sizes, depending on concentration. Chandler and McBain,[2] state that "presumably at any given concentration a dynamic equilibrium establishes as large number of species of particles, dominated by a few species that comprise the major concentrations."

In opposition to this view, Hartley[3][4][5] assumes no such change of micellar size with concentration. He considers that the aggregate has a well-marked optimum size and composed of 50-100 paraffin chain ions. This aggregate he states "is formed from single ions with a very low concentration of intermediate aggregates."

Yet another approach has been made by Meyer and van der Wyk.[6] These workers have applied the Mass Action Law to the building up of a large micelle from simple ions and consider, in opposition to Hartley's views, that appreciable concentrations of intermediaries must exist.

The question of micellar charge is as disputed as the associated one of micellar size. Chandler and McBain, in their recent paper, consider a maximum of four charges even in the largest aggregate, a view not inconsistent with McBain's earlier contention that the charges on the micelle surface were so far apart that

they behaved as though independent.[7] Hartley holds that large interionic effects exist and that charges are so close that the micelle simulates a multivalent ion. A further postulate is necessary, namely that ions of opposite charge ("gegenions") adhere to the micelle to explain the observed conductivity and transport number values on this theory.

The existence of large interionic effects has been shown to be highly probable by the measurements of Malsch and Hartley[8] of conductivity at high field strengths and those of Schmid and Larsen[9] of conductivity at high frequencies. It is with the results of these latter workers that we are concerned here.

Conductivity measurements at high frequencies may give noticeably higher results than similar measurements carried out with slowly changing or stationary fields. This rise at high frequency was predicted theoretically by Falkenhagen[10] for ordinary electrolytes and confirmed by many workers. He explains that on an average any ion will be surrounded by an atmosphere of ions of predominantly opposite sign and when the central ion moves in a stationary field, this ion atmosphere which tends to move in the opposite direction will exert a retarding force. By the application of a sufficiently rapidly changing field, the ionic

atmosphere will be unable to re-form round the central ion to exert its full retarding effect. Consequently, a conductivity increase will be observed at high frequencies, of magnitude dependent upon the magnitude of the interionic effects.

Measurements of the conductivity of various colloidal electrolytes at high frequencies and at different concentrations should thus give useful information as to the role of these interionic effects in aqueous solutions of colloidal electrolytes. In addition, Schmid and Larsen[9] obtained, in sodium dodecyl sulphate solutions below the critical concentration, a 3% effect which they attributed to dipole absorption. If it existed, further investigation should provide useful information on the state of colloidal electrolyte solutions below the critical concentration. Complete failure to reproduce these results or others above the critical concentration at their stated frequencies necessitated re-examination of some of their work and a considerable extension of the frequency range employed. Higher concentrations of colloidal electrolyte were also examined.

References.

(1) Lingafelter, Chem.Rev., 44, 135, (1949).

(2) Chandler and McBain, J.Phys. and Coll.Chem., 53, 930, (1949).

(3) Hartley, "Aqueous Solutions of Paraffin-chain Salts," Herman et Cie., Paris (1936).

(4) Hartley, Koll.Z., 88, 33, (1939).

(5) Hartley, Quarterly Reviews, 2, 152, (1948).

(6) Meyer and van der Wyk, Helv.Chim.Acta, 20, 1321, (1937).

(7) McBain, "Colloid Chemistry," (Alexander), Vol.5, 102, (1944).

(8) Malsch and Hartley, Z.phys.Chem., A170, 321, (1934).

(9) Schmid and Larsen, Z.f.Elektrochem., 44, 651, (1938).

(10) Falkenhagen, "Electrolytes," 211, Oxford, (1934).

Preparation of Materials.

Sodium dodecyl sulphate. A sample of sodium dodecyl sulphate, manufactured by Henkel and Co., Dusseldorf, was recrystallised twice from water and three times from methyl alcohol; then dried in a desiccator over calcium chloride. The value of the equivalent conductivity of a 0·01M aqueous solution of the salt at 25 deg.C. did not agree with the results of other authors.[1][2][3] This fact and the existence of discrepancies of the order of 10% between the results of these investigators at a concentration of 0·01M at 25 deg.C., indicated the need for accurate measurement of the low-frequency conductivity.

The purity of the sodium dodecyl sulphate was suspected and it was decided to carry out analyses of the material for comparison with corresponding conductivity determinations. 15 Mls. of 1:3 Analar dilute hydrochloric acid and about 100 mgm. of sodium dodecyl sulphate were allowed to simmer for two hours. After dilution to 100 mls. total volume, 15 mls. of hot 5% barium chloride solution were added to the hot solution, which was allowed to stand for a further two hours. The precipitate, washed twice

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(1) Howell and Robinson, Proc.Roy.Soc.Series A, 155, 386 (1936).
(2) Lottermoser and Puschel, Kolloid Z., 63, 175 (1933).
(3) Schmid and Larsen, Z.f.Elektrochem., 44, 651 (1938).

by decantation was transferred to a sintered glass crucible and washing with water continued until the filtrate was free from chloride. To remove traces of dodecyl alcohol, the precipitate was further treated with two 5 ml. portions of hot alcohol. Heating at 130 deg.C. in an air oven for half an hour was necessary to dry the precipitate, before cooling and weighing.

Repeated determinations by this method revealed large inconsistencies due, possibly, to the presence in the barium sulphate of dodecyl alcohol from the hydrolysis.(1)

It was thought that dodecyl alcohol present in varying amounts in the original solid, could be responsible for the inconsistencies mentioned above. Some of the compound was therefore extracted for twentyfour hours with dry 40-60 deg.C. petrol ether in a Soxhlet extractor,(2) modified so that the thimble was always drained of the extracting liquid. No change in the analysis or conductivity could be detected.

To eliminate the possibility that the commercial preparation of sodium dodecyl sulphate was impure, the compound was made from dodecyl alcohol (Schuchardt, Gorlitz) by the following method.(3) 112 Gms. of

(1) Compare Lottermoser and Stoll, Kolloid Z., 63, 49, (1933).
(2) Miles and Shedlovsky, J.Phys.Chem., 48, 57 (1944).
(3) Ward, J.Chem.Soc., 522 (1939).

primary normal dodecyl alcohol, m.p. 24·5-25·5 deg.[1] C., were acted on, with constant mechanical stirring by 76 gms. of chloro-sulphonic acid, added dropwise over a period of 2½ hours, the temperature being maintained at 40-45 deg.C. The product was poured with stirring into 300 mls. of water containing 30 gms. of sodium hydroxide. The solid which separated on cooling the solution in ice, was filtered off and recrystallised once from water. Cooling and subsequent rapid filtration at the pump resulted in high recovery of the compound. After a further three recrystallisations from aqueous ethyl alcohol (commercial, absolute), the yield was about 60 gms. of sodium dodecyl sulphate.

The conductivity figures being virtually identical with those obtained with sodium dodecyl sulphate from commercial sources, some of the compound from the above preparation was extracted as before with 40-60 deg.C. petrol ether. Again no change in conductivity was noted.

The consistency of the conductivity figures seemed to throw doubt on the analysis figures. The ignition method of Ward[2] was now tried, with complete success, and was adopted in preference to the sulphate precipitation method. About 0·2 gms. of sodium dodecyl sulphate were weighed out in a

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(1) Heilbron, "Dictionary of Organic Compounds"(1943) gives 25 deg.C. p.1069.
(2) Ward, J.Chem.Soc., 522 (1939).

previously ignited and weighed silica crucible and lid. The solid was carefully ignited with frequent raising of the lid in the early stages. When most of the volatile material had been driven off and the bottom of the crucible was at a dull red heat, the lid was removed and ignited separately. All traces of carbon were burned from the walls of the crucible which was turned in the pipe-clay triangle to allow all parts to be treated similarly with the Meker burner. The lid was then replaced and the white solid residue heated to fusion point. After cooling in a desiccator for thirty minutes and allowing to stand in the balance case for a further ten minutes, the crucible and residue were weighed. The sulphuric acid treatment recommended by Ward (loc.cit.) was found unnecessary. An analysis at this stage gave 7·81(1)% sodium at this stage (theory requires 7·976%).

A re-examination of the literature revealed that Ward (loc.cit.) reported that sodium dodecyl sulphate, which had been standing for some months over phosphorus pentoxide gave an analysis of 7·973% sodium, Intensive drying seemed, therefore, to be required. This was carried out in a drying-pistol under vacuum at 60 deg.C., with phosphorus pentoxide as desiccant. Analyses were carried out at different stages as

given below.

Drying period in hours.	Sodium determinations.
0	7.81(1)%
3½	7.88(6)%
5½	7.90(5)%
20	7.97(3)%

No decomposition took place, since no period of drying, however long, yielded a sodium percentage greater than theoretical. Samples of sodium dodecyl sulphate, previously dried, showed a noticeable increase in weight even on standing for periods of some minutes.

All samples of sodium dodecyl sulphate employed in determination of conductivity were dried for at least twentyfour hours, before use. A high-vacuum pump was later used in preference to the water pump to evacuate the drying apparatus.

Sodium Hexadecyl Sulphate. 72 gms. of primary normal hexadecyl (cetyl) alcohol, M.P. 56-57 deg.C.[1] were acted on by 37 gms. of chloro-sulphonic acid, added dropwise with constant mechanical stirring, at

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(1) Heilbron "Dictionary of Organic Compounds" gives M.P. 49 deg.C. on p.413 (under cetyl alcohol) but see Philips & Mumford "The Dimorphism of Certain Higher Aliphatic Compounds" J.C.S., 1732 (1931). The delay in change from one form to the other may give an erroneously high determination.

60-65 deg.C.[1] over a period of two hours. The brownish product was poured into 15 gms. of sodium hydroxide in 150 mls. of water, stirred, allowed to stand in a refrigerator overnight and filtered. Recrystallisation four times from aqueous alcohol (commercial, absolute) yielded an almost white, granular solid. Solutions of the product in water alone were found to be cloudy. Unchanged cetyl alcohol being the most likely impurity, the salt was extracted for some days with 40-60 deg.C. petrol ether. On further recrystallising from aqueous alcohol, white glistening plates of sodium hexadecyl sulphate, similar in crystalline form to those of the corresponding dodecyl sulphate, were obtained. A preliminary drying period in an air over, was followed by grinding of the crystals to a fine powder in an agate mortar and subsequent drying under vacuum in a drying-pistol for at least twentyfour hours.

A micro analysis by Messrs. Weiler and Strauss gave the following results.

	Required.	Found.
Carbon	55·78%	56·2%
Hydrogen	9·66%	9·63%
Sulphate	27·89%	25·5%

(1) Lottermoser & Stoll, Kolloid Z., 63, 49 (1933) use conc. sulphuric acid at 50-70 deg.C.

Cetyl Pyridinium Chloride. Attempts were made to obtain this compound by recrystallising cetyl pyridinium bromide[1] from dilute hydrochloric acid (Hartley)![2] Recovery of the compound was only accomplished with difficulty and yields were very small. An alternative method was tried with success.

Hydrochloric acid gas was passed into a solution of cetyl pyridinium bromide in about 50 mls. of dioxan contained in a large U-shaped tube. Large volumes of the gas were rapidly absorbed, the form of the receiver preventing any sucking back. Quantities of cetyl pyridinium bromide were added from time to time. After two hours, additions were discontinued, but hydrochloric acid gas was passed in for a further hour. The solution was then cooled with ice, the solid filtered off and repeatedly recrystallised by dissolving in dioxan, adding acetone and cooling in ice![3] Extraction with 40-60° petrol ether followed by recrystallisation from acetone alone was subsequently found to improve the form of the crystals. The compound was dried in a drying pistol for 24 hours at 60°C. and exposed to the

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(1) Product of Messrs. Imperial Chemical Industries (Dyestuffs Division).
(2) Hartley, J.A.C.S., 58, 2347 (1936).
(3) Hauser and Miles, J.Phys.Chem., 45, 954 (1941).

atmosphere in a tube in the balance-case. For the purpose of making up solutions this compound was reckoned as the monohydrate though this is somewhat uncertain. Melting-point (80-83°C.) was identical with that found by other investigators[1] but a moisture content determination yielded a low result (2·8%, monohydrate requires 5·05).

On this basis, one would expect that the low-frequency conductivity measurement would be somewhat higher at a given concentration than those found by other investigators. In fact, as is shown in the discussion, the present measurements are lower. The discrepancies may be due to conducting impurities.

The yield of the above method was not measured directly but the efficiency of conversion of cetyl pyridinium bromide to the chloride was extremely high. The greatest losses were incurred in repeated recrystallisations.

Potassium Chloride:- Two samples (from different sources) of "Analar" quality potassium chloride were dried by heating slowly and then to the point of fusion, in a porcelain basin held in a piece of

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(1) Shelton, van Campen, Tilford, Lang, Nisonger, Bandelin and Rubenkoenig, J.A.C.S., 68, 757 (1946).

asbestos board through which a suitable size of hole had been punched. The basin was in direct contact with the flame, while its contents were protected from contamination.

Identical weights of the two samples were dissolved in the same quantity of water. The resistance values of these solutions in the same cell were identical. This was taken as sufficient indication that no further purification was needed. Potassium chloride, for standardisation purposes, was kept in a desiccator until required.

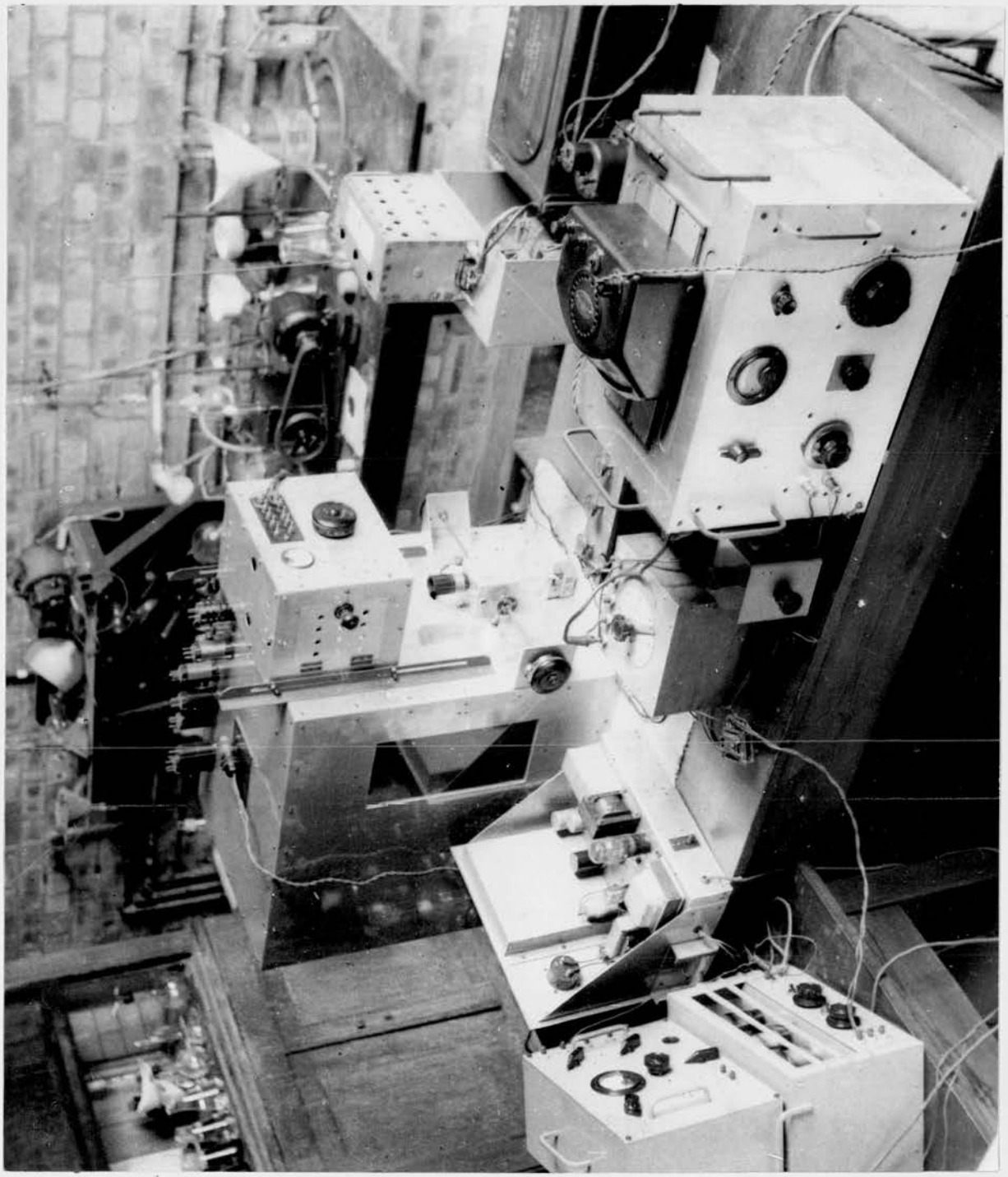
Conductivity Water. For measurements of the low-frequency conductivity of solutions of sodium dodecyl sulphate, water was prepared by the use of a Vogel and Jeffery[1] still. While water of various specific conductivities, often below 1 gemmho, was initially obtained, when it had come to the correct temperature in the air thermostat, it reverted to a value of about 2 gemmhos. The indications were that this was a value for equilibrium with the carbon dioxide inevitably present in the thermostat and derived, it was thought, from oxidation of the

(1) Vogel and Jeffery, J.C.S., 1201 (1931).

carbon brushes of the air-circulating motor.

Apparatus.

Fig. 1.



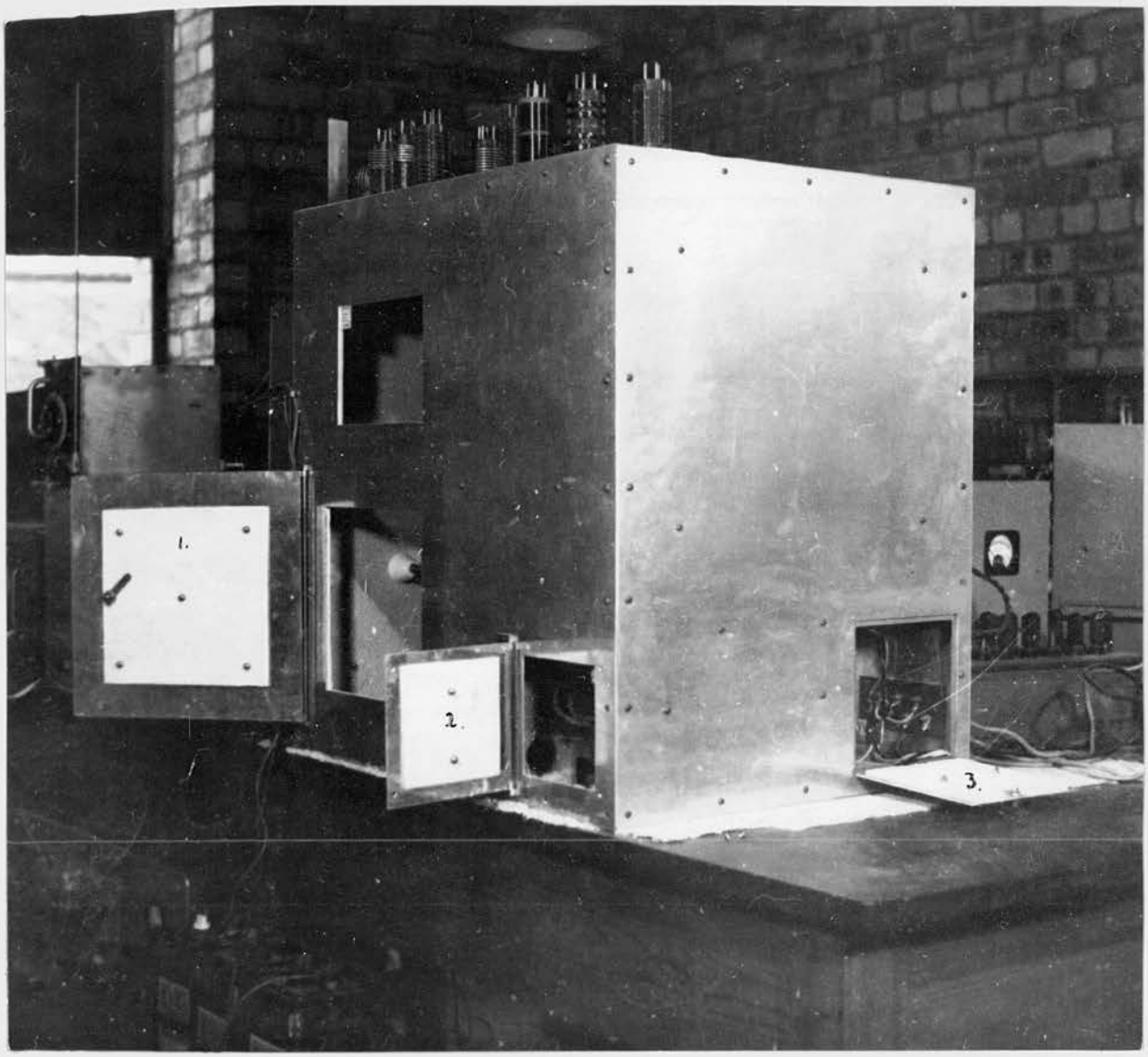
General.

The complex apparatus which the nature of the present investigation necessitated was constructed from its component parts by the writer. When work was started, apparatus of the type required was in short supply and, although some of the equipment was available as commercial products, it could not be readily acquired. In other cases, no comparable equipment had been made previously and here, of course, there was no alternative but to construct.

Undoubtedly, the time-consuming nature of this construction work left proportionately less time for experimental investigations, but, when modifications to the apparatus were required - these were many and forced upon him - the writer had circuit diagrams and the necessary knowledge of the "inner workings" at hand. The costs, too, of what would otherwise have been an expensive research, were reduced to a minimum, extensive use being made of the large amount of equipment, surplus to War Department requirements, which, while of little value in its original state, provided an ample store of components, especially valves.

Fig. 1. is a photograph of some of the equipment constructed.

Fig. 2.


1.
2.
3.

Temperature Control.

The difficulties of accurate temperature control are multiplied many times in high-frequency conductivity work, compared with investigations at low - or audio - frequencies. The use of water as a thermostatic medium, while having disadvantages at low frequencies,[1] is inadmissible at these high frequencies, where the glass walls of the conductivity cell act, not so much as an insulator, but as a dielectric and produce an alternative path for the high-frequency currents. The high-frequency losses in a substance such as oil are by no means negligible and there is little choice of material other than air as a thermostatic medium. An air-thermostat was therefore constructed.

The Thermostatic Tank. The thermostatic tank employed in this work is shown in Fig. 2. It is built mainly of aluminium sheets, 16 s.w.g., secured by brass screws on a framework of brass angle, one inch broad and tapped with the appropriate thread. This metal-work forms a very effective electrostatic screen for the cell inside, making measurements independent of body-capacity effects.

Heat insulation is accomplished by an internal lining of "uralite", a type of asbestos board.

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(1) Jones and Josephs, J.A.C.S., 50, 1049 (1928).

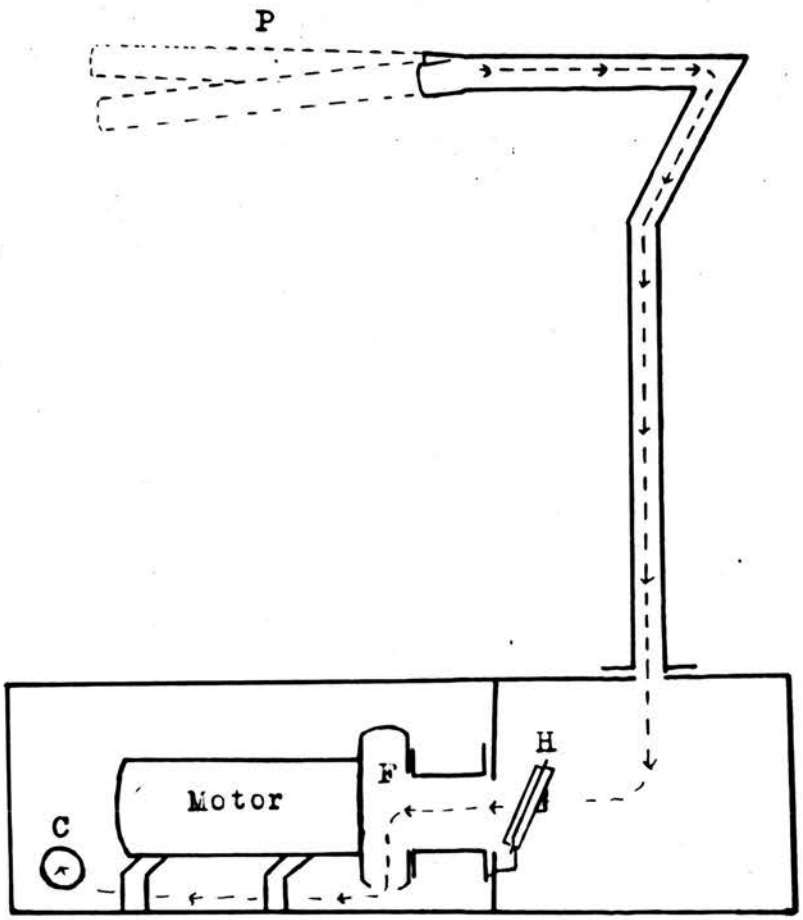
Inside the frame, where such a lining would be difficult to fit, cotton wool (as shown in Fig. 12, a view taken through the main thermostat door) has been glued for heat insulation purposes. As will be seen from the photograph, Fig. 2, the doors are backed by "uralite". The main door (1) at the front, which allows access to the cell, is mounted on specially made hinges. A substantial overlap between this door and the front of the thermostat ensures that the former is reasonably air-tight. Other doors permit ready removal of the circulating motor (2) and access to the heating chamber (3).

A small observation window at the front enables the temperature of the thermostat to be observed on an internally suspended thermometer. At the rear of the thermostat a larger window provides general illumination.

Circulating and Heating Systems. For close control of temperature, the air must be well stirred and local heating avoided. The heating source must not be appreciably hotter than the surrounding material and should preferably be separated from direct contact with the air in the main chamber of the thermostat.

Attention is paid to these points in the specially designed circulating system (Fig. 3.).

Fig. 3.



Circulating System.

Air passes from the main chamber of the thermostat through a Y-shaped pipe (P) of perforated zinc (the air-stream is broken up and thoroughly mixed by this arrangement) into a copper pipe which leads to the heating chamber. There the air is drawn, by an electric fan (F), over a heater (H), made of nickel-chrome wire wound on two mica strips crossed at right angles. On its ejection from the fan-housing, the air circulates over the rear of the motor, cooling the portion containing the commutator. Experiment showed that such cooling was desirable, considerable heat being generated by the friction of the carbon brushes on the commutator. A copper pipe (cross-section C.) conveys the air from the motor chamber to the centre of the floor of the thermostat, where it is returned, through a pipe of perforated zinc, to the main chamber.

Regulation. It was realised at the outset that the air-thermostat would be difficult to control. The high specific heats of a mercury regulator and of normal types of heating system, relative to the very small specific heat of the air, rendered the temperature liable to fluctuate between wide limits. Modification of the heating system, from a large lamp to the type noted above, resulted in some

improvement but control was still far from satisfactory. It was obvious that the mercury regulator required to gain too much heat in order to shut off the heater and to lose too much heat before switching it on again. This demanded an appreciable temperature gradient between the regulator and the surrounding air - a condition which was inconsistent with good temperature regulation.

It has been known for some time that the resistance of a fine wire, which is supported so that it is mainly in contact with the air and not with the former, on which it is wound, can follow rapid temperature fluctuations.(1) The writer found copper wire, (40 s.w.g. enamelled) wound on a hexagonal coil-former, to be satisfactory for such a controlling device.

Two methods are available to operate the relay from the variation of resistance with temperature. An alternating or a direct current bridge may be employed. While the latter leads to greater simplicity,(2) (3) (4) much greater sensitivity can be obtained by the former.

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(1) Yates, J. Sci. Instr., 23, 229 (1946).
(2) Zabel and Hancox, Rev. Sci. Instr., 5,28(1934).
(3) Hirst and Cannon, J. Sci. Instr., 20, 129 (1943)
(4) Wright, J. Sci. Instr., 24, 258 (1947).

The reason lies in the ability of valves to amplify the out-of-balance alternating voltage supplied from the Wheatstone alternating-current bridge. Comparable amplification of a direct voltage is difficult without introducing unnecessary complications. Hence to obtain the sensitivity required for sufficiently close control of temperature in the present instance, an alternating-current bridge is employed.

It is common practice with a.c. bridge-operated thermostatic controls to introduce some form of phasing-system so that the operating current through the relay does not increase or decrease on either side of the bridge balance-point but increases on one side and decreases on the other. The phasing systems of Yates (1) and Coates (2) were attempted but the regulator was found to operate most satisfactorily without a phasing-voltage.

Despite the introduction of the electronic regulator there was a distinct tendency to "hunt", (3) mainly on account of the heating element being above

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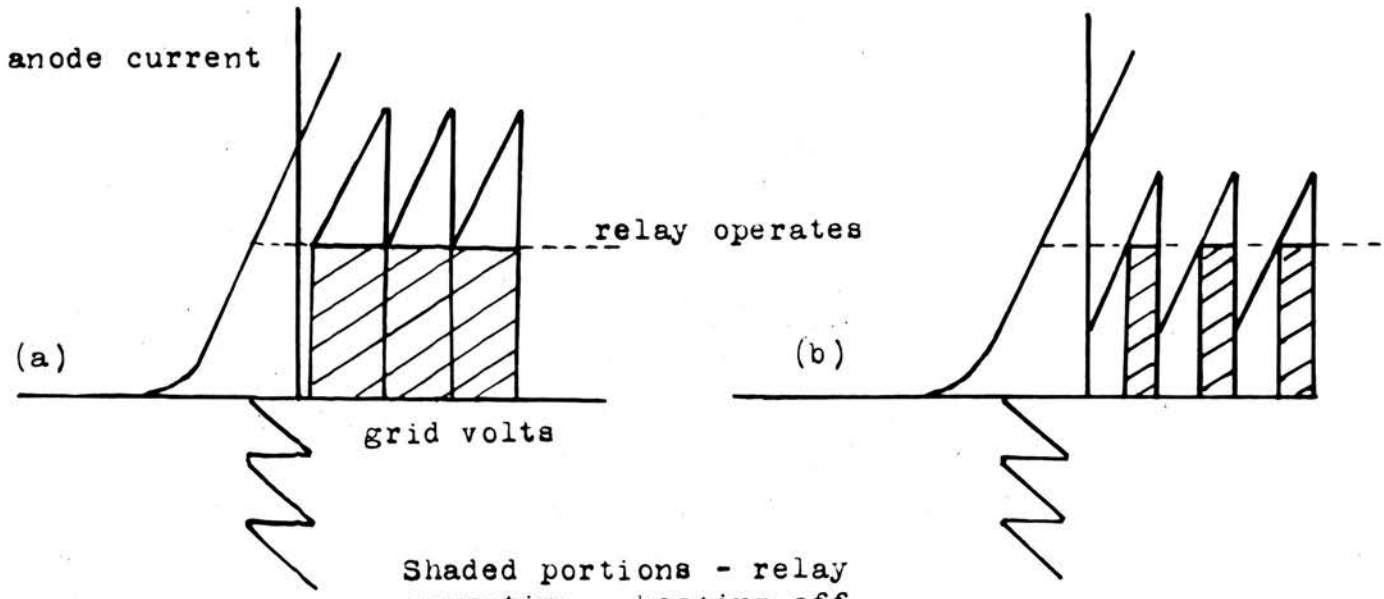
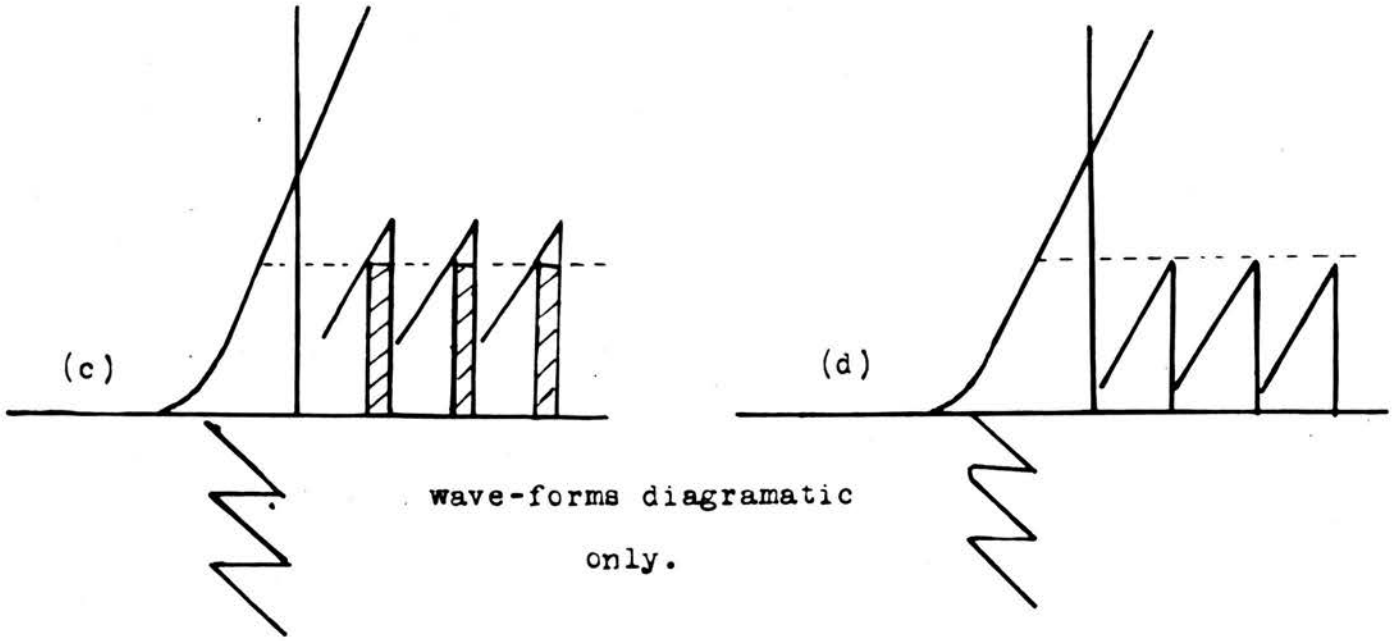
(1) Yates, J. Sci. Instr., 23, 229 (1946).
(2) Coates, J. Sci. Instr., 21, 86 (1944).
(3) Hoselitz, J. Sci. Instr., 22, 96 (1945).

Fig. 4 (a), (b) (c) and (d)

Thermostat Cooling.



Shaded portions - relay operative - heating off.



wave-forms diagramatic only.

the thermostat temperature when the control switched off the heating current. The heater was capable of supplying a further quantity of heat sufficient to raise the thermostat above the desired temperature. This could only be overcome by some form of continuous control. Coates[1] recommends the use of a saturable-core choke or transformer but these would require fairly large operating currents. Hoselitz[2] introduced a system whereby the control was shut off and on periodically. Sunvic Controls Limited,[3] in their Electronic Proportioning Resistance Thermometer, have devised a system in which the ratio of time-on to time-off of the relay (and hence of the heating) is proportioned to temperature. The time of one complete cycle of operation is 30 secs. which is far too long to control the present thermostat properly. Since none of the existing designs of control appeared able to regulate the thermostat efficiently, a new system was devised.

The Principle of the Regulator. The relationship between grid voltage and anode current (the mutual characteristic) for a triode valve, is shown in Fig.4(a). If a relay is in the anode circuit, as soon as the negative bias becomes small enough, the

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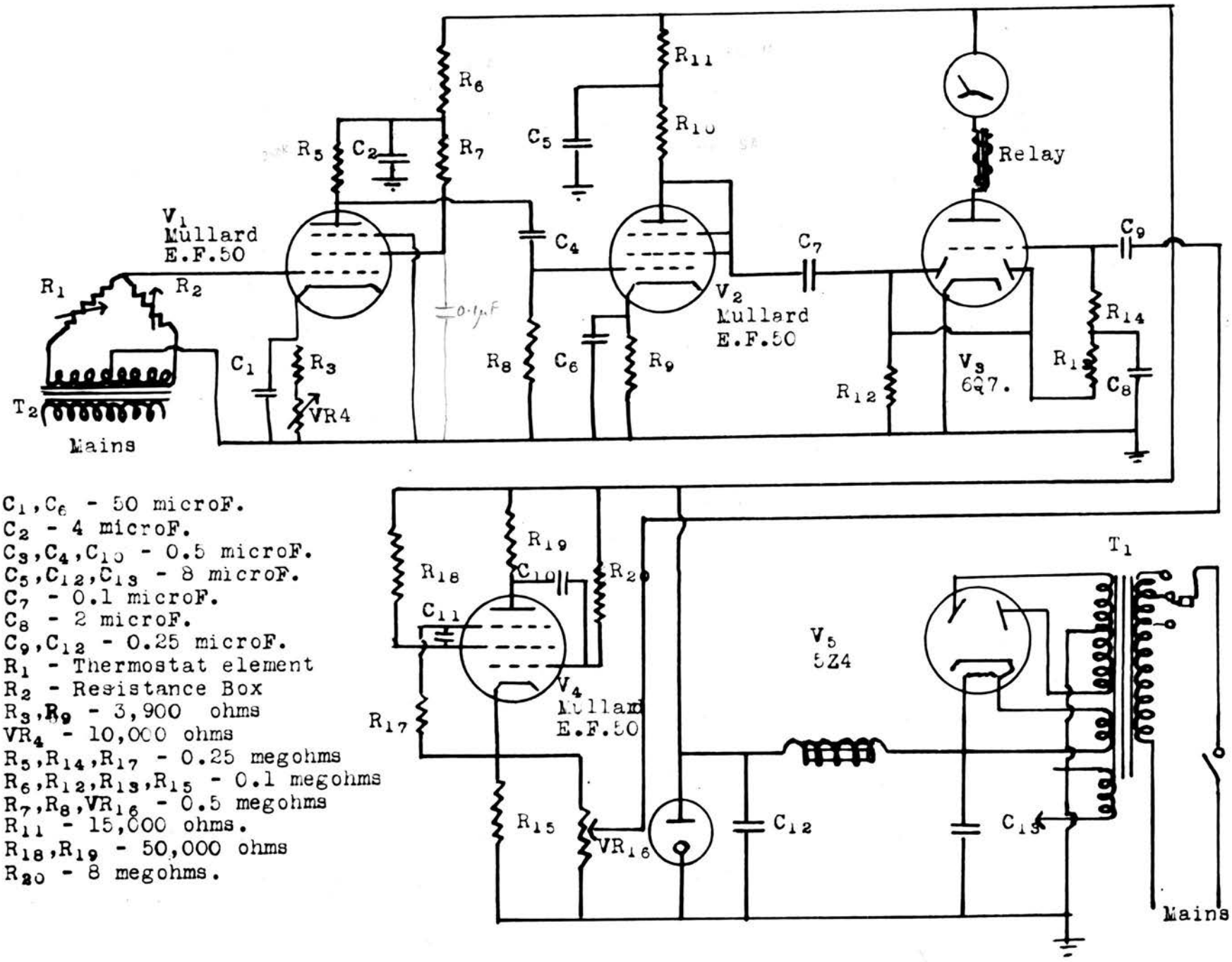
(1) Coates, J. Sci. Instr., 21, 86 (1944).
(2) Hoselitz, J. Sci. Instr., 22, 96 (1945).
(3) Sunvic Controls Limited, J. Sci. Instr., 24, 277 (1947).

Fig. 5.

The Thermostat Regulator.



C_1, C_6 - 50 microF.
C_2 - 4 microF.
C_3, C_4, C_{10} - 0.5 microF.
C_5, C_{12}, C_{13} - 8 microF.
C_7 - 0.1 microF.
C_8 - 2 microF.
C_9, C_{12} - 0.25 microF.
R_1 - Thermostat element
R_2 - Resistance Box
R_3, R_9 - 3,900 ohms
VR_4 - 10,000 ohms
R_5, R_{14}, R_{17} - 0.25 megohms
$R_6, R_{12}, R_{13}, R_{15}$ - 0.1 megohms
R_7, R_8, VR_{16} - 0.5 megohms
R_{11} - 15,000 ohms.
R_{18}, R_{19} - 50,000 ohms
R_{20} - 8 megohms.

anode current will be sufficiently great to cause it to operate and it will do so each time these conditions prevail provided that the duration of the operating pulse is large compared with the time the relay requires to open and close. The fraction of the time the relay is closed to the time it is open will thus depend on the fraction of the time the grid is sufficiently positive. This fraction may be varied as shown in Fig. 4 b, c and d, by varying the steady valve of the grid bias on which the periodic fluctuation is superposed. If this steady value is controlled by the temperature in the thermostat, the ratio of time-on to time-off of the relay can be proportioned so that the heat supplied to the thermostat is just sufficient to maintain the desired temperature.

A similar method of control of pulse-width appears to have been used in connection with Signalling Equipment No. 10.(1) As far as the writer is aware, this method of controlling a thermostat has never been tried previously.

The Regulator. The circuit employed is shown in Fig.5. V_1 and V_2 amplify the out-of-balance voltage from the bridge which is formed by the centre-tapped

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(1) A description is given in Wireless World, 52 187 (1946.)

secondary of T_2 and the resistors R_1 and R_2 and which is supplied by a 50 c/s alternating voltage, about 5 v. in amplitude. R_2 is a resistance-box whose valve is adjusted so that balance is obtained just above the thermostat operating temperature. Initially, the bridge is out of balance and the amplified voltage is rectified by the diodes of V_3. The negative potential resulting is applied via R_{13} and R_{14} to the grid of V_3 whose anode current is cut off when the bridge is far out of balance. Under these conditions, the heating is on and the relay inoperative. Approaching balance, the negative potential applied to V_3 rapidly diminishes, the anode current rises and the heating is switched off. Fine control of temperature may be obtained by varying the gain of V_1, by adjusting the value of the cathode resistor VR_4.

V_4 is a single valve time-base[1] of the transition type[2] which has been modified to produce a positive-going saw-tooth waveform at the cathode[3]. The amplitude of the saw-tooth, which determines the steady bias variation necessary for complete variation in heating pulse-length, can be controlled by the potentiometer VR_{16}.

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(1) Fleming-Williams, Wireless Eng., 17, 161 (1940).
(2) Puckle, "Time Bases", 4th Imp. 41 (1945).
(3) Cooking, Wireless World, 52, 176 (1946).

Performance of the Control. The present instrument is capable of controlling the air thermostat to about plus or minus one hundredth of a degree Centigrade, provided the mains voltage is constant to a few volts and the room temperature does not vary within wide limits. Large variations of mains voltage affect the voltage applied to the bridge through T_2 and are amplified by V_1 and V_2. To help to combat these fluctuations the control is supplied with current through an a.c. mains stabiliser, though it would be better to supply the bridge portion from an amplitude-controlled oscillator.

Much greater amplification could be obtained from V_1 and V_2. This cannot be utilised in practice since the balance-point obtainable with the present bridge circuit is insufficiently sharp. The out-of-balance potential, with full sensitivity, never becomes small enough to make the negative voltage on V_3 diminish, to allow the relay to operate. These improvements could readily be effected but are hardly necessary at present.

The regulator, in its present form, has proved itself capable of overcoming the difficulties involved in maintaining a temperature, sufficiently constant for the present investigation, in the air-thermostat.

The Determination of Conductivity at High Frequency.

Choice of Method. In choosing a method of determining high-frequency conductivity, frequency range, conductivity range, ease of operation and accuracy have all to be considered.

On the basis of the previous work of Schmid and Larsen[1], a frequency range of up to 25 megacycles per second (Mc/s) was at first considered sufficient. With a conductivity cell to the design of Schmid and Erkkila,[2] a cell resistance of 3000 ohms was thought to be a suitable lower limit. The transitron oscillator[3][4] meets these requirements and is easy to operate, since its amplitude of oscillation can be controlled by a single potential, the control grid bias.[5] The coils are simple to construct and readily interchanged for different frequency ranges.

As soon as the oscillator was complete, an attempt was made to check the results of Schmid and Larsen[1] on sodium dodecyl sulphate.

Alternative methods of operating the transitron oscillator were available, one of which was based on

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(1) Schmid and Larsen, Z. f. Elektrochem. 44, 651 (1938)
(2) Schmid and Erkkila, Z. f. Elektrochem. 42, 737 (1936)
(3) Brunetti, Proc. Inst. Rad. Eng., 25, 1595 (1937)
(4) Brunetti, Proc. Inst. Rad. Eng., 27, 88 (1939)
(5) Williams, Wireless World, 50, 241 (1944).

finding the grid-bias voltage at which the tuned circuit and conductivity cell (in parallel) commenced to oscillate. By determining the appropriate grid-bias voltages for various solutions of potassium chloride of known resistance in the cell, the relationship could be established at a given frequency, between resistance and grid bias voltage. If now the solution whose high-frequency resistance was to be determined was substituted in the cell, a grid bias voltage could be similarly found at which the circuit commenced oscillation and the corresponding high-frequency resistance ascertained from this relationship. An attempted confirmation of Schmid and Larsen's work for 0.025 M sodium dodecyl sulphate at 25 deg. C. completely failed. There was, at most, a small uncertain increase in the conductivity.

Although it was not clear that the method was at fault, the following alternative method was tried. The grid-bias voltage was kept constant at a value permitting weak oscillations in the circuit[1] with the cell connected and filled with potassium chloride solution of known resistance. The amplitude of oscillation was measured by a high-frequency valve-voltmeter (described later). Determinations of

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(1) Deubner, Phys. Z. 30, 946 (1929).

amplitude with other potassium chloride solutions of different resistance enabled an amplitude vs. resistance graph to be drawn. The oscillation amplitude with 0.025M sodium dodecyl sulphate solution in the cell was determined. The value of the high-frequency resistance derived from the graph again failed to correspond to that of Schmid and Larsen.

Failure to account for these discrepancies on the basis of inaccurate low-frequency determinations, led the author to the conclusion that these workers unwittingly used frequencies higher than those reported. It was therefore decided to carry out determinations at higher frequencies.

At these frequencies it is advantageous to adopt the resonance method similar to that employed by Mizushima[1] and by Sack,[2] owing to the difficulty, at higher frequencies of maintaining oscillations in a tuned circuit damped by the resistance of the conductivity cell. Two separate circuits are required for the resonance method, a high-frequency oscillator and a resonant circuit with associated means of measuring voltage across it.

The High-frequency Oscillator. For successful operation of the resonance method, the high-frequency oscillator must be of reasonable power, otherwise the

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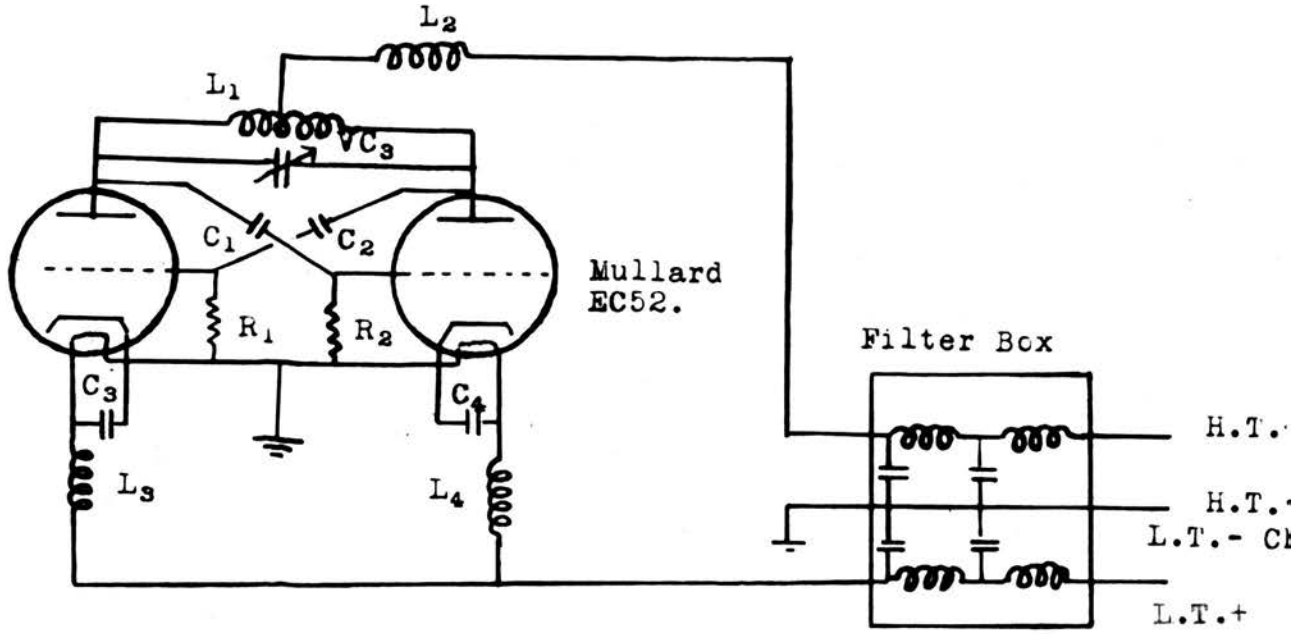
(1) Mizushima, Bull. Chem. Soc. of Japan, 1, 47 (1926)
(2) Sack, Phys. Z., 29, 627 (1928)

Fig. 6 (a) and (b)

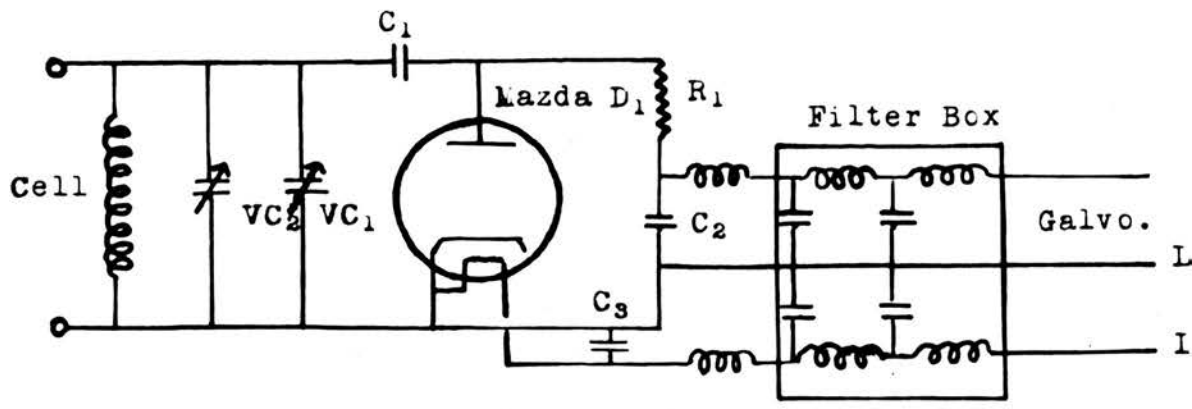
Oscillator Circuit.



$R_1 = R_2 = 10{,}000$ ohms
$C_1 = C_2 = 50$ pF.
$C_3 = C_4 = 25$ pF.
$VC_3 = 160$ pF.

Fig. 6(a)

Resonant Circuit.



$C_1 = C_3 = 50$pF.
$C_2 = 1000$pF.
$VC_1 = 100$pF.
$VC_2 = 10$pF.
$R_1 = 220{,}000$ ohms.

Fig. 6(b).

voltage induced in the auxiliary circuit will be too small for accurate measurement with a coupling between them which is not excessive. This requirement was met by using two valves in "push-pull", which had the advantage of leading to virtual cancellation of the high-frequency currents in the high-tension supply.(1)

The valves chosen for the oscillator are VR137's, the Service equivalent of Mullard EC52's. They are designed specially for use at ultra-high frequencies and are stated to be capable of oscillation up to 400 Mc/s, though, in the present circuit, they were employed up to 70 Mc/s only. When initially set up the oscillator was found to be prone to "squegging", a phenomenon which was readily detected by picking up the high-frequency oscillation on the receiver (described below). A complete cure was accomplished by reducing the grid resistors R_1 and R_2 (Fig. 6a) to their present value.

Resonant and Detector Circuits. Separate from the oscillator circuit is a tuned circuit composed of a coil and two tuning capacitors in parallel. Since tuning is very critical, one of these is used for coarse adjustments only and final adjustments are carried out by the other. Both are connected to

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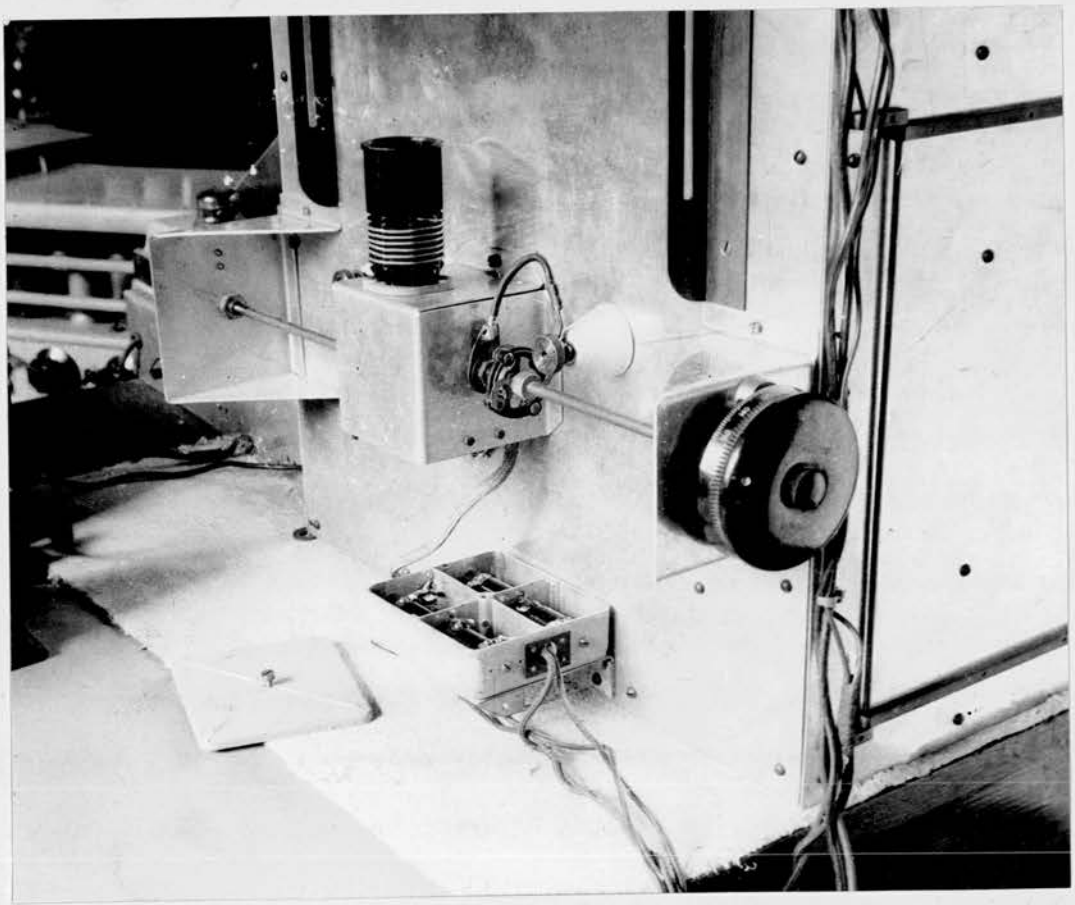
(1) A full description of the circuit (Fig. 6a) is given in Hartshorn, "Radio-frequency Measurements by Bridge and Resonance Methods" 4th. Imp., p.73 (1947).

Fig. 7.



flexible couplers which are actuated by Muirhead slow-motion drives. The method of construction is indicated in Fig. 7.

The coil, with which the cell is in parallel, is loosely coupled to the oscillator. Coupling may be increased by moving the latter on a slide of brass angle (the lower portion of this slide may be observed on the thermostat wall in Fig. 7) towards the coil. Occasionally, coupling was too close for the permitted traverse of the oscillator. When this occurred, coupling was reduced by the insertion of an aluminium plate, with a large circular hole in its centre, on the underside of the oscillator frame.

The potential across the coil is determined by means of the diode D1 (Fig. 6b) which rectifies a portion of the total circulating current, and this, in turn, deflects a spot galvanometer. This deflection is the quantity measured.

Precautions at Higher Frequencies. As Hartshorn[1] points out, it is advisable to insert a high-frequency choke in the high-tension supply lead, to allow for slight inequalities in the operation of the two valves. In addition to this choke L_2, chokes L_3 and L_4 were inserted in each filament supply lead to eliminate unwanted couplings between valves.

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(1) Hartshorn, loc. cit.

At frequencies greater than about 20 Mc/s, even the shortest leads possess inductance and leads which apparently run direct to the chassis ("earth") may affect the operation of the circuit profoundly. To reduce these possible troubles to vanishing point and to confine the high-frequency currents to the chassis round the valve-base, two insulated, silver-plated brass rings were fitted concentrically with both valve-bases. All "earth" leads were taken to these rings which were connected to chassis at one point only.(1)

Even with all these precautions, slight changes in galvanometer deflection (measuring voltage across the resonant circuit) were noted when the operator touched certain leads. An aluminium screen, inserted between the oscillator and resonant circuits did not reduce this deflection to zero, proving that coupling was taking place by means other than through the tuning coils. A complete cure was effected by inserting filter units, composed of small high-frequency chokes and by-pass capacitors in separate compartments of aluminium screening boxes, in all leads (other than "earth" leads) in the oscillator and resonant circuits.(2) One of these filter units, (with the lid removed for purposes of the photograph)

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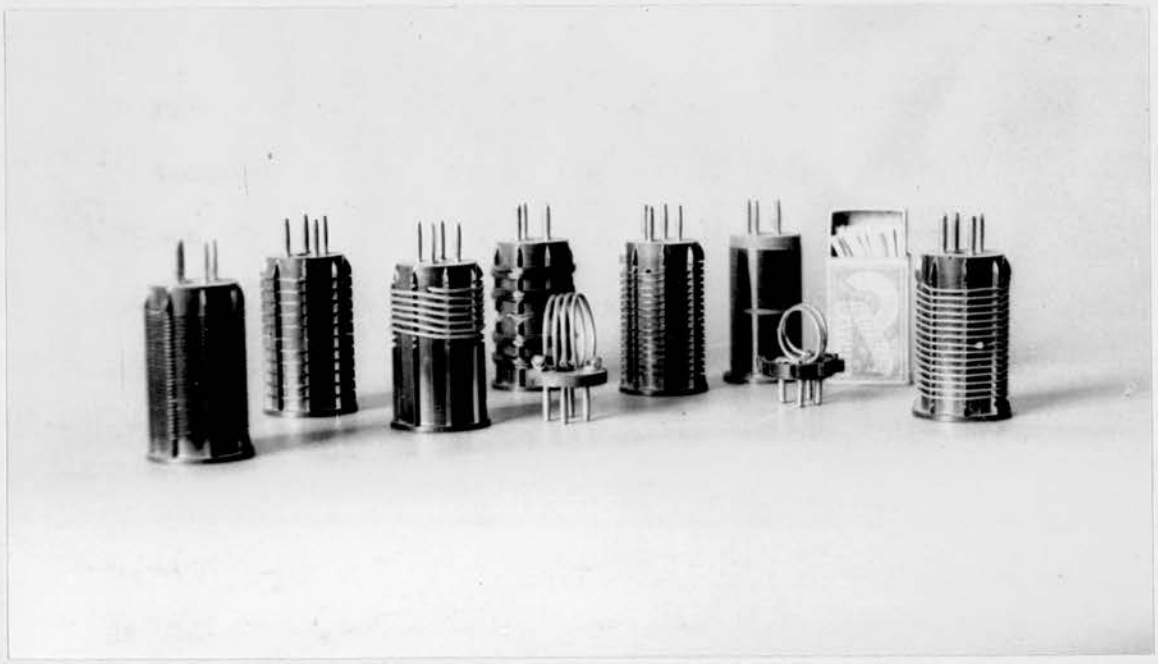
(1) Zepler, "The Technique of Radio Design", 3rd. Imp., Chap. 8., 183 (1945)
(2) Beattie and Knight, Wireless World, 50, 66 (1944).

Fig. 8.



may be seen below the resonant circuit in Fig. 7.

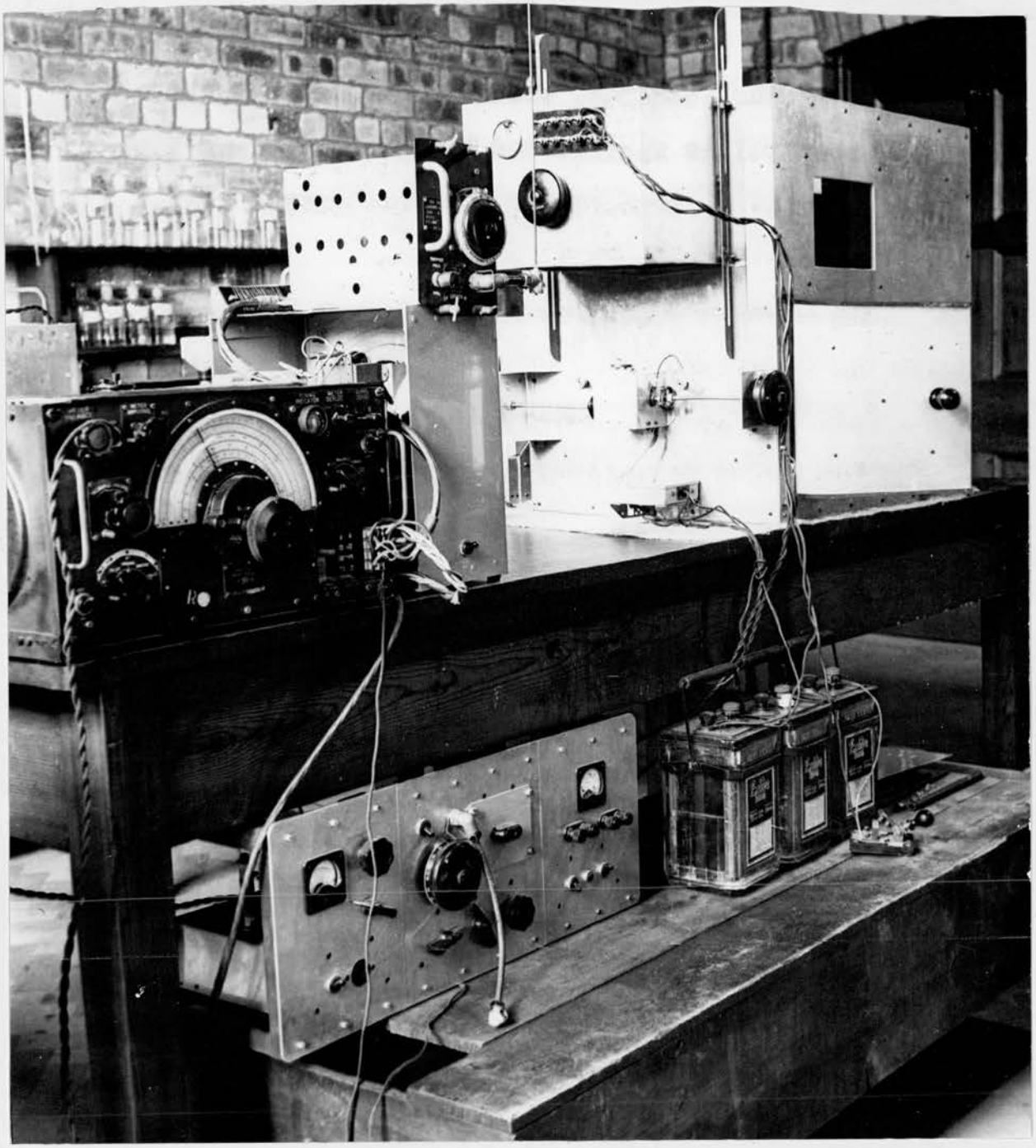
The precautions enumerated, together with the method of mounting on the thermostat wall, resulted in complete freedom from any effect due to the proximity of the operator and rendered unnecessary any of the methods of remote control adopted by some workers.

Coils. A selection of the coils used is illustrated in Fig. 8. These coils are of the interchangeable plug-in type, to enable the apparatus to work over a wide frequency-range. The only difficulty experienced was corrosion and faulty contact of the pins, a difficulty which was overcome by periodic cleaning with fine emery paper.

Frequency-determining Equipment. From an examination of the experimental results, it will be appreciated that, because of the nature of the conductivity/frequency relationship, accurate determination of frequency is a very essential requirement. The equipment, shown in Fig. 9, consists of three distinct parts, a receiver, a converter and a calibrating oscillator.

The calibrating oscillator, seen immediately below the receiver in Fig. 9, consists of a 100 kc/s crystal-controlled oscillator and harmonic amplifier with optional low-frequency modulation. The harmonics of this oscillator can be detected by the

Fig. 9.



receiver up to at least 10 Mc/s (the 100th) and serve to calibrate the receiver in this way. Accurate setting of the receiver, which is an R1155 (an Air Ministry type) is facilitated by observation of the diminution of shadow-area in the "magic-eye" tuning indicator with which it is equipped.

The converter, an Air Ministry Type 26, tunes over the frequency range 50 to 66 Mc/s and provides an output at 7.5 Mc/s which is detected by the R 1155 receiver, tuned to this last frequency.

Calibration. Receiver, converter and high-frequency oscillator were switched on for about thirty minutes prior to calibration. For frequencies up to 10 Mc/s, calibration of the receiver with the calibrating oscillator is straightforward, the settings at which the harmonics of the 100 kc/s oscillator are received with maximum strength being noted. For frequencies between 10 and 18 Mc/s, the limit for the receiver, the high-frequency oscillator is tuned to frequencies of 5.5, 6.....9 Mc/s by picking up the appropriate harmonic of the calibrating oscillator on the receiver and altering the high-frequency oscillator tuning until zero beat is obtained. When receiver tuning is changed, the corresponding second harmonics can be detected at 11, 12.....18 Mc/s.

In a similar manner, the converter may be calibrated by receiving the weak higher harmonics of the

Fig. 10 and 11.

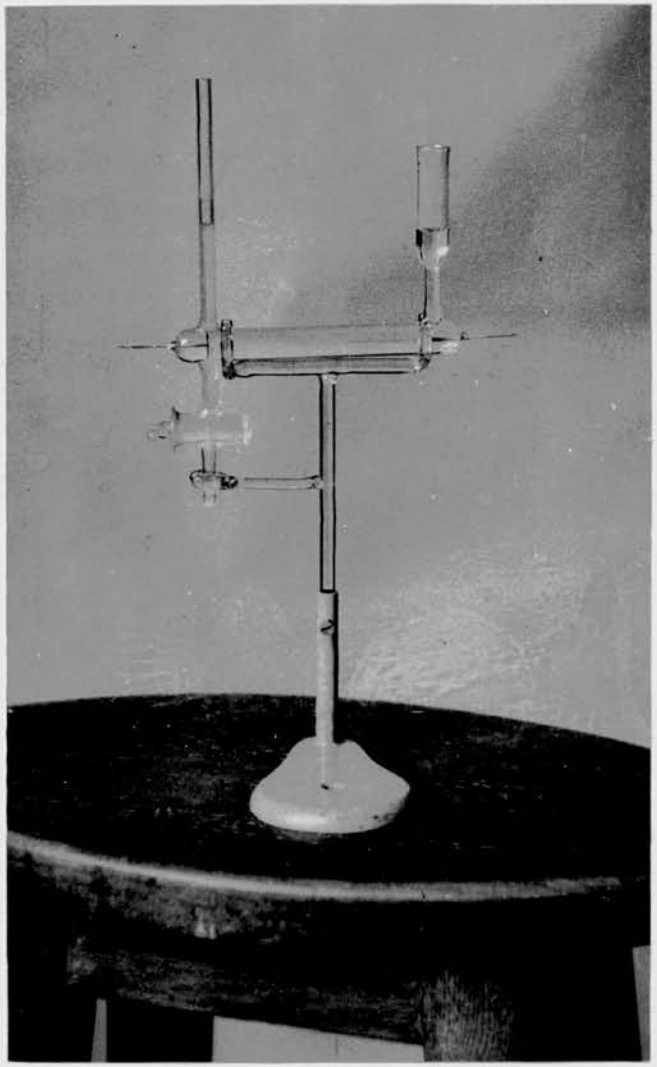


Fig. 10.

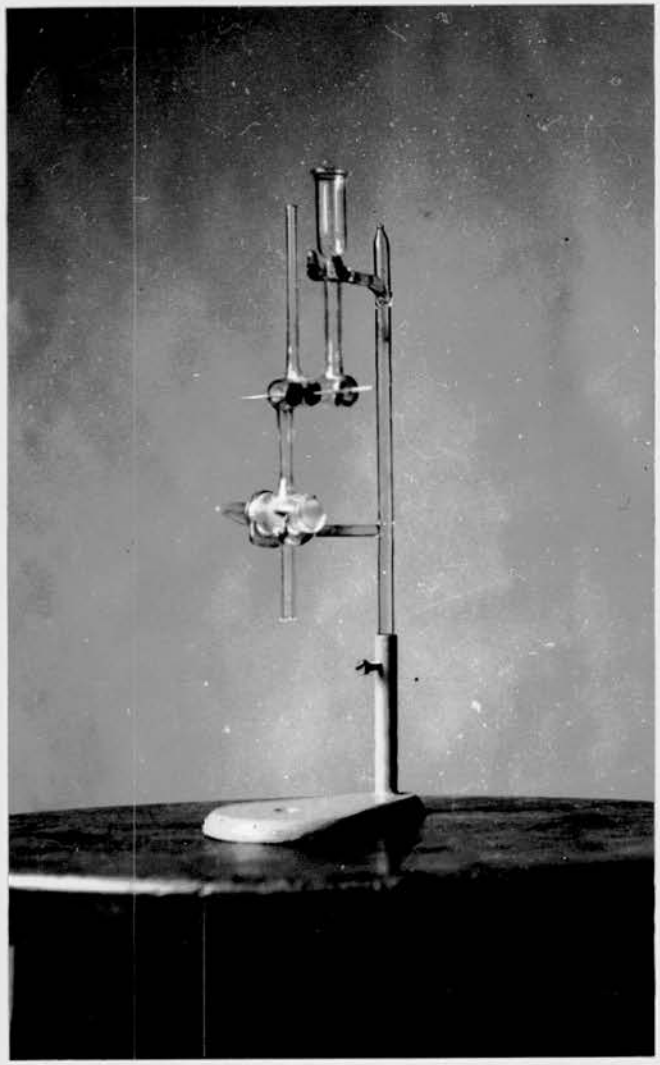


Fig. 11.

high-frequency oscillator, which, when set at say 11 Mc/s will give signals detectable at 55 and 66 Mc/s on the converter scale.

There exist frequencies for which these methods are inapplicable. For a frequency of 35 Mc/s, for instance, there is no corresponding point on the main receiver or converter scales. In this case, the high-frequency oscillator is set to 17.5 Mc/s with respect to the receiver, the coupling between the high-frequency oscillator and resonant circuits is increased and, with a suitable coil in the resonant circuit, a setting of its tuning capacitors can be found which produces a small but readily detectable galvanometer deflection. The resonant circuit is now at 35 Mc/s, the second harmonic. If the oscillator coil is now changed and the coupling substantially reduced, a much larger deflection is observed when the oscillator also is exactly tuned to 35 Mc/s. The oscillator setting is noted.

The methods outlined above enabled the frequency of the oscillator to be checked at intervals of about 2 Mc/s over the range 9 to 70 Mc/s.

Conductivity Cells for High Frequencies. Photographs of the two cells for use at high frequencies (Figs. 10 and 11) reveal that these are similar in construction and are both supported on glass stands which fit

Fig. 12.

the same base. Each has a filling tube, a levelling tube, with a fine mark to reproduce levels, and a tap by which each may be emptied. The bore of the central tube is large enough to accommodate the grey platinum electrodes which are 1 cm. in diameter. In the first cell, Fig. 10, these are 10 cm. apart and in the second, Fig. 11, only 1 cm. The former cell is a duplicate of that used by Schmid and Larsen.(1)

A further cell (3) used to facilitate low-frequency measurements is of normal construction and will not be described in detail.

Cell Mounting and Connections. Fig. 12 is a view taken through the thermostat door with cell (1) in position. Spring crocodile clips, attached to short leads which are, in turn, brought through the thermostat wall by large "frequentite" insulators, make connection to the plates of the cell. This compact assembly which requires extremely short leads, is well illustrated by Figs. 12 and 7, views of opposite sides of the same thermostat wall.

High Tension Supply. Good reproducibility of the high-tension supply voltage, of the order of 70 volts, is absolutely necessary to fix the oscillator output. This voltage is obtained from the mains by the power-pack, described below, whose circuit is shown in Fig.13.

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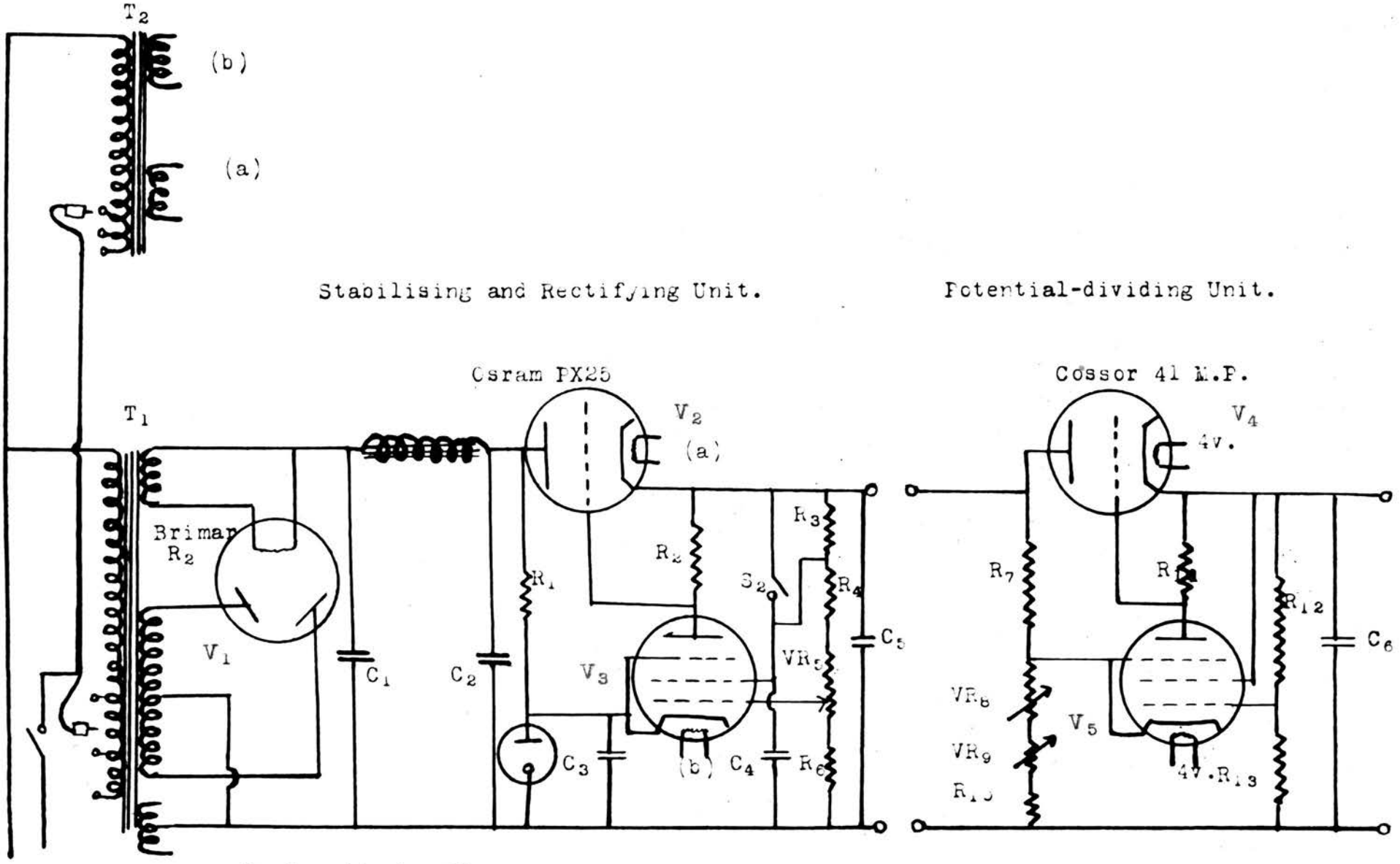
(1) Schmid and Larsen, Z. f. Elektrochem., 44, 651 (1938)

Fig. 13.



C_1, C_2 - 16 microF.
C_3 - 2 microF.
C_4, C_5, C_6 - 8 microF.

R_1, R_{11} - 0.5 megohms.
R_2 - 0.2 megohms.
R_3 - 20,000 ohms.
R_4, R_{12} - 10,000 ohms.
VR_5 - 15,000 ohms.

R_8, VR_8, R_{10} - 5000 ohms.
R_7 - 0.1 megohms.
R_{13} - 500 ohms.

The cathode of the controlling valve V_3 is maintained at a practically constant potential by the neon lamp. The grid voltage for V_3, obtained from a potential-dividing network across the output from the stabilising and rectifying unit, is of such a value that normally the grid is slightly negative with respect to the cathode. An increase in the output voltage, whether brought about by an increase in mains voltage or a decrease in the current supplied to the load, causes the grid to become relatively more positive. The anode current of V_3 therefore increases and causes a larger voltage drop across the anode load resistor. This increased voltage drop is applied to the grid of V_2, whose anode current decreases. The voltage drop across V_2 correspondingly increases, decreasing the voltage externally available and compensating for the original voltage rise. Switch S_2, when closed, raises the screen-grid and control-grid potentials of V_3 and increases its anode current which produces a greater bias on V_2 and an increased voltage drop across this valve, so that the output voltage is very much diminished.

Unfortunately, the voltage derived from the stabilising and rectifying unit cannot be less than the striking voltage of the neon lamp incorporated in the cathode circuit of V_3. To overcome this difficulty, a potential dividing unit was constructed.

The unit operates in the same way as the stabilising circuit except that accurate control of the output voltage is obtained by varying the cathode voltage of V_5, the grid voltage being fixed. Component values for the unit were arrived at by experiment.

As shown by the circuit diagram (Fig. 13) of both units, the heater voltages for two valves are derived from individual windings on transformers; for the other two better results were obtained by supplying heaters from accumulators. A common heater supply for all valves V_2 to V_5 is inadmissible because their respective cathodes are at a high potential above "earth" and there is a strong possibility of breakdown of the heater-cathode insulation.

The units described do not provide perfect stabilisation but the voltage can always be manually adjusted to an accurately reproducible level. Better and more elaborate circuits have been developed recently.(1)

Low Tension Supplies. A 6 volts supply, for the oscillator valves and the voltage-measuring diode of the resonant circuit, was provided by three two-volt accumulators. High-frequency filters, which have already been mentioned, were inserted in the positive leads to the oscillator valves and the diode to eliminate unwanted coupling between their respective

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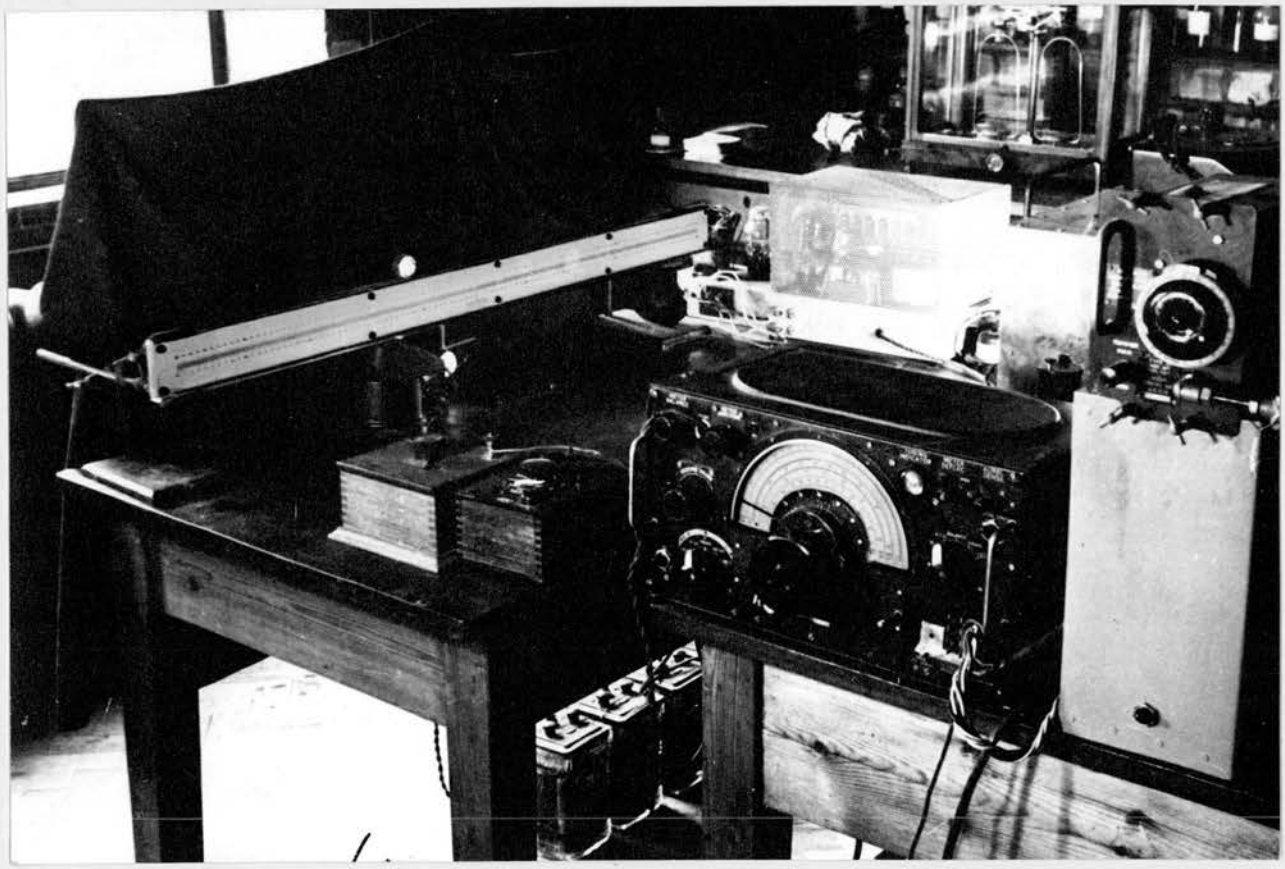
(1) Scroggie, Wireless World, 54, 373, 415, 453 (1948)

Fig. 14.



circuits.

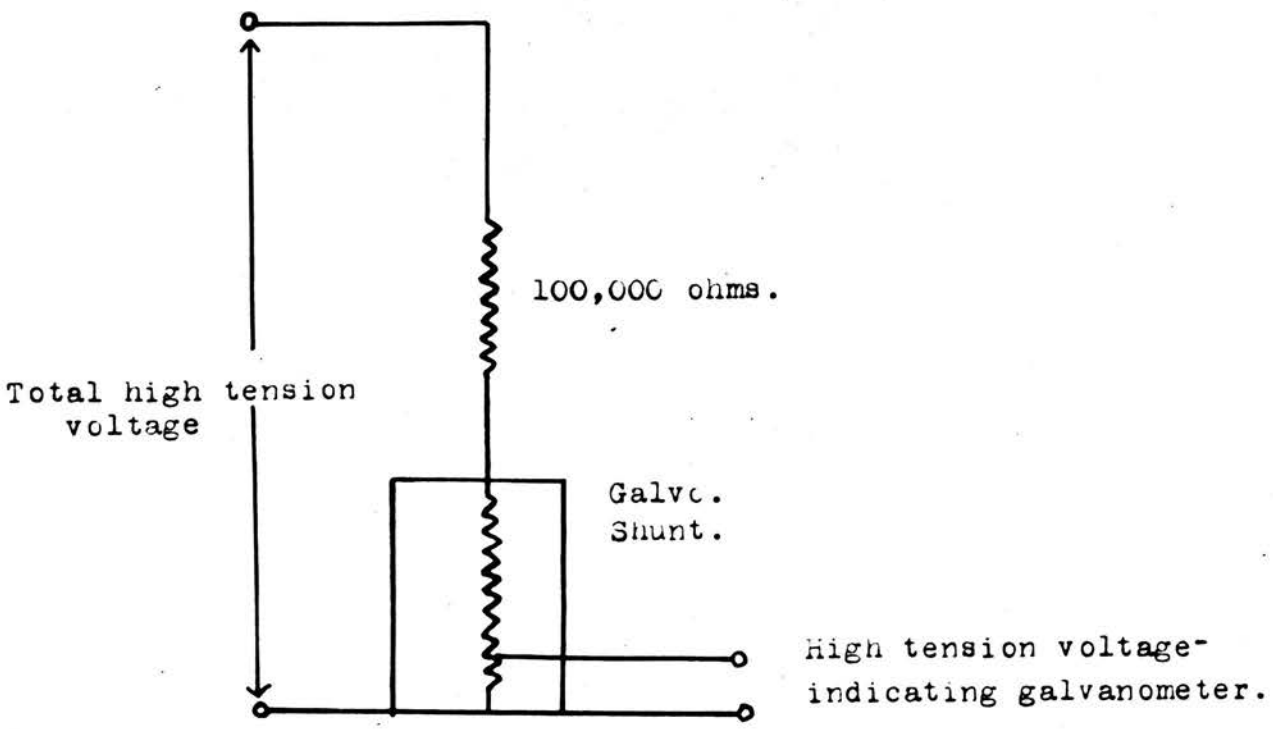
Resonant Circuit and High Tension Voltage Indicating Systems.

The high tension voltage must be reproduced at a given value each time the resonant circuit galvanometer deflection is to be read. After many experiments had been performed in which these quantities were determined by different instruments, the author conceived the idea of projecting both deflections on the same scale so that they could be read simultaneously. Higher accuracy and greater speed resulted.

The metre scale, with both spots in representative positions is shown in Fig. 14.

To obtain comparable deflections, a minute fraction of the high tension voltage is all that is required. The voltage dividing network of Fig. 15 accomplished this object admirably. During experiments the high-frequency oscillator was switched off, by interrupting the high tension supply, in order to determine the resonant circuit galvanometer zero. The high tension system, however, remained on and its galvanometer therefore continuously deflected, eliminating any necessity for determination of the zero.

Fig. 15.



Voltage dividing network for high tension voltage indicating galvanometer.

The Determination of Conductivity at Low Frequency. Although the problems associated with the determination of conductivity at low frequencies have been extensively treated elsewhere (in particular, the work of Jones and co-workers)[1], they reappeared in an accentuated form when high resistances had to be determined in the present work.

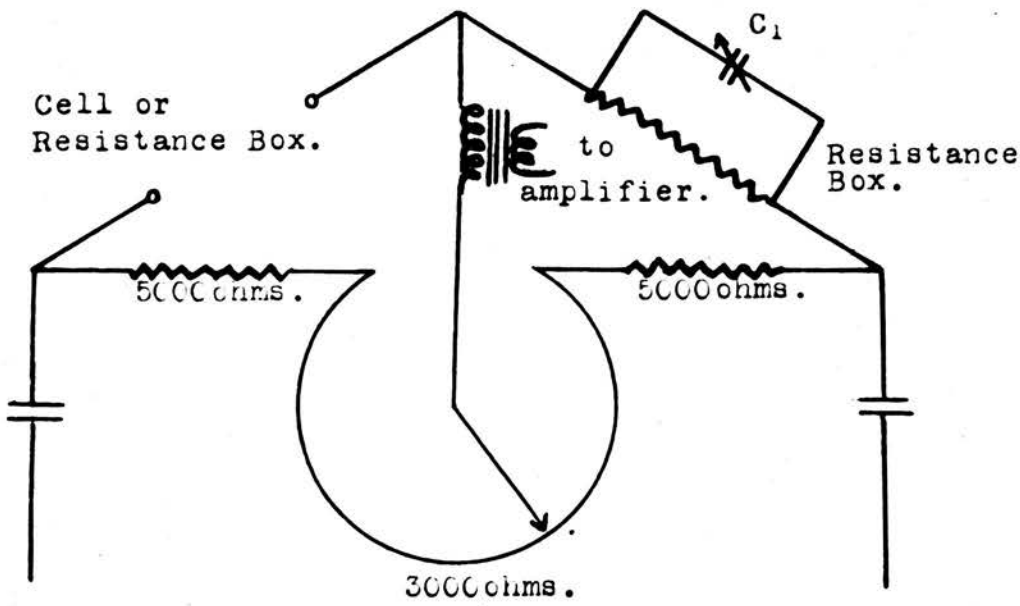
With the conventional slide-wire bridge and ordinary resistance boxes, it is practically impossible to obtain a sharp minimum at these high resistances. A further difficulty arises because the normal type of bridge possesses a low resistance and cannot be used with advantage with the heat-frequency oscillator (described below), as the optimum load for this instrument is of the order of thousands of ohms.

In view of these considerations, a low-frequency bridge was specially constructed, consisting of a large, circular, wire-wound potentiometer of 3000 ohms resistance, connected at each end to a 2 watt carbon resistor (5000 ohms).

As carbon resistors have an appreciable temperature coefficient, this may be considered open to criticism, but the bridge is always used at ratios not far from unity, when such resistance changes tend to cancel out both in the resistors themselves and in

(1) Jones and co-workers, J.A.C.S., 50, 1049 (1928), 51, 2407 (1929), 53, 411, 1207 (1931), 55, 1780 (1933) 57, 272, 280 (1935), 59, 731 (1937) and 62, 2919 (1940).

Fig. 16


C_1
Cell or
Resistance Box.
to
amplifier.
Resistance
Box.
5000 ohms.
5000 ohms.
3000 ohms.
To Oscillator.

the potentiometer. A scale (which can be calibrated directly in ratios) is mounted beneath the potentiometer control knob.

Despite the use of this form of bridge, good balance-points could not be obtained when the resistances in the arms of the Wheatstone network were greater than 1000 ohms (provided by the ordinary type of resistance box). It was noticed that the balance-point was always better using the "hundreds" switch set at "10" than with the "thousands" switch set at "1". This was taken to mean that capacitances in the resistance box were responsible for the poor balance-point.[1] (the capacitance with many individual resistors in circuit is less than with a single large resistor of similar value, because of physical separation). When a variable air-capacitor was put in short with one of the resistance boxes (the exact one being determined by experiment), as in Fig. 16, an excellent balance-point was obtained up to values of 10,000 ohms.

On substituting the "ten-thousands" switch set to "1" for the thousands switch set to "10", in an ordinary resistance box, the capacitor in the opposite arm of the bridge had to be increased to about 2000 pF, from about 100 pF previously necessary for a good balance-point.

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(1) Jones and Josephs, J.A.C.S., 50, 1049 (1928).

To minimise the effects of capacities in the resistance boxes at still higher resistance values, a small resistance box was built up of small resistors of the type employed in radio receivers. These have minute shunt-capacitance and behave excellently over the entire audio-frequency range (Terman[1]). Unfortunately, the small temperature coefficient of the resistors is not negligible and their powers of heat dissipation, because of their small size, are low. The former difficulty can be overcome by calibration using direct current immediately after use in the alternating current bridge; the latter does not arise as the current through the bridge is extremely small.

The need for very frequent calibration is a disadvantage and, while for resistances greater than 20,000 ohms the carbon resistors were always used, for the bulk of measurements between 10,000 and 20,000 ohms a specially wire-wound resistance of negligible temperature coefficient was employed in series with an ordinary box for subdivision. The wire on this special resistor was sectionally wound, on a flat "tufnol" strip, in twenty slots (to minimise capacity effects) with reversal of the direction of winding at each slot (to cancel inductive effects).

Both the bridge and the resistors were calibrated

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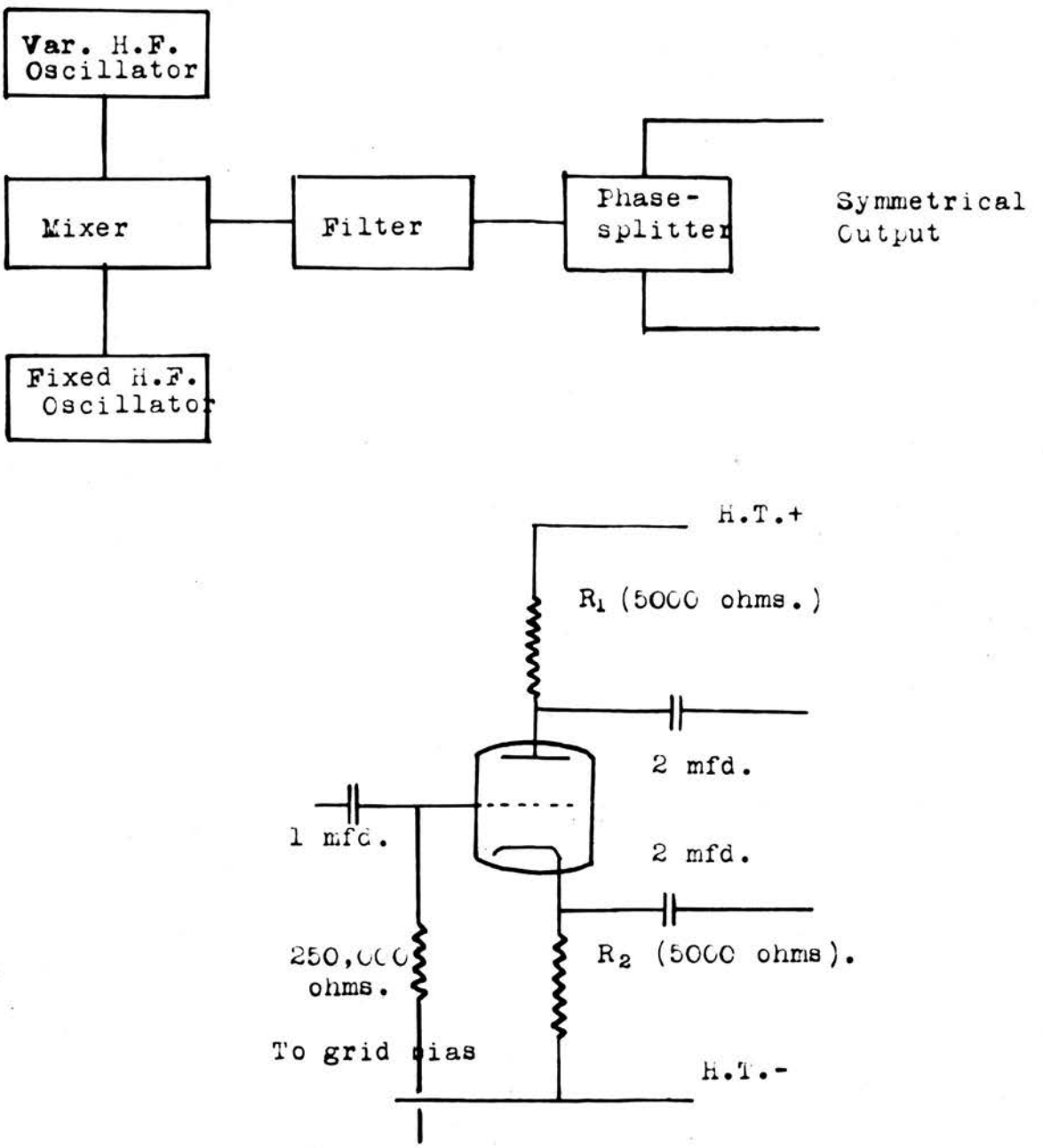
(1) Terman, "Radio Engineers Handbook", 1st Ed. 41 (1943)

Fig. 17 and 18.



The Phase-splitter.

against standard resistance boxes (accuracy better than 1 in 1000) with direct current. The indicating instrument was a Cambridge spot galvanometer.

A Wagner ground[1][2] of the type used by Jones and Josephs[3] was incorporated in the bridge. The symmetrical form of the output circuit from the oscillator (described below) renders the use of such a ground hardly necessary.

The Low-frequency Source. A beat-frequency oscillator (B.F.O.) provides the source of low-frequency oscillations to energise the bridge. As pointed out by Terman[4], a properly constructed heat-frequency oscillator has practically sinusoidal waveform and an output independent of frequency, which in turn can be readily controlled. For the present work, the fact that large ranges of frequency can be covered rapidly, facilitates testing of resistance boxes and the low-frequency bridge itself for frequency dependence and enables the frequency applied to the bridge to be chosen at will.

The oscillator itself (shown schematically in Fig. 17) which was specially constructed and modified for the present work, consists of two high-frequency,

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(1) Taylor and Acree, J.A.C.S., 38, 2396 (1916).
(2) Morgan and Lammert, J.A.C.S., 48, 1232 (1926).
(3) Jones and Josephs, J.A.C.S., 50, 1058 (1928).
(4) Terman, "Measurements in Radio Engineering", 1st. Ed. 298, (1935).

resistance-stabilised oscillators (Terman[1]) of about 100 ke/s, whose oscillations are combined in a triode-hexode mixer valve[2]. The resultant beat-note, from which the high-frequency components are removed by a filter, is passed to a "phase-splitter"[3], in order to obtain a symmetrical output. This markedly improves the sharpness and accuracy of the balance-point.

As shown in Fig. 18, the filtered, audio-frequency voltage is applied to the grid of the phase-splitter valve. The resulting fluctuations in current produced in the equal resistances R_1 and R_2, give identical voltages at the anode and cathode of the valve. These, however, are opposite in phase, since the anode becomes more negative and the cathode more positive, as the grid becomes more positive. The potentials are applied to the bridge via the capacitors C_1 and C_2.

Calibration. Despite the fact that no frequency-dependence of conductivity could be established at low frequencies, it was considered desirable to calibrate the oscillator and always determine the low-frequency conductivity at 1000 c/s.

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(1) Terman, "Measurements in Radio Engineering", 1st. Ed. 283 (1935).
(2) Scroggie, "Radio Laboratory Handbook", 2nd Ed. 51.
(3) Puckle, "Time Bases", 4th Imp. 115 (1945).

For calibration purposes, the mains 50 c/s voltage (through a transformer) was made to describe a circle on the screen of a small cathode-ray tube.[1] The output voltage from the beat-frequency oscillator, applied to the grid of the cathode-ray tube modulated the brilliance of the trace. A stationary circle composed of spots was observed whenever the B.F.O. and mains voltages were simply related. The relationship, number of spots X 50 frequency, was used to calibrate the B.F.O. at every multiple of 50 c/s.

The Bridge Balance-point Amplifier. Headphones normally function as bridge balance-point detectors but, with high resistances it becomes difficult to hear the very weak sounds,[2] especially if other apparatus, causing even a small amount of sound, is in use.

Transformer-coupled amplifiers were employed by early investigators to obtain high amplification but the rapid improvement in valves in recent years renders transformers unnecessary and resistance-capacitance coupling has been employed throughout the present amplifier. A great advantage gained is that such an amplifier has a more uniform response with

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(1) Terman "Measurements in Radio Engineering" 1st. Ed. 328 (1935)
(2) Glasstone, "The Electrochemistry of Solutions", 2nd Ed. 59 (1937)

different frequencies[1][2] and practically immune from stray pick-up troubles.

A symmetrical input circuit was tried, similar to that used in biological amplifiers,[3] but seemed to be influenced unduly by the stray capacitances associated with the bridge.[4] A symmetrical input transformer was substituted, with complete success. The present amplifier, constructed on conventional lines, is a three-stage, mains-driven type and will not be described in detail.

Even with the use of an amplifier, the sensitivity of indication with headphones or loudspeaker is markedly diminished at extreme audible frequencies and in the presence of extraneous sounds. A visual indication of balance is better in this case and is provided by a valve voltmeter which measures the output voltage of the amplifier.

The Valve Voltmeter. The main object of the valve voltmeter was to provide a visual indication of balance but, on occasions, the need arose for a very sensitive indicator of the presence of high-frequency

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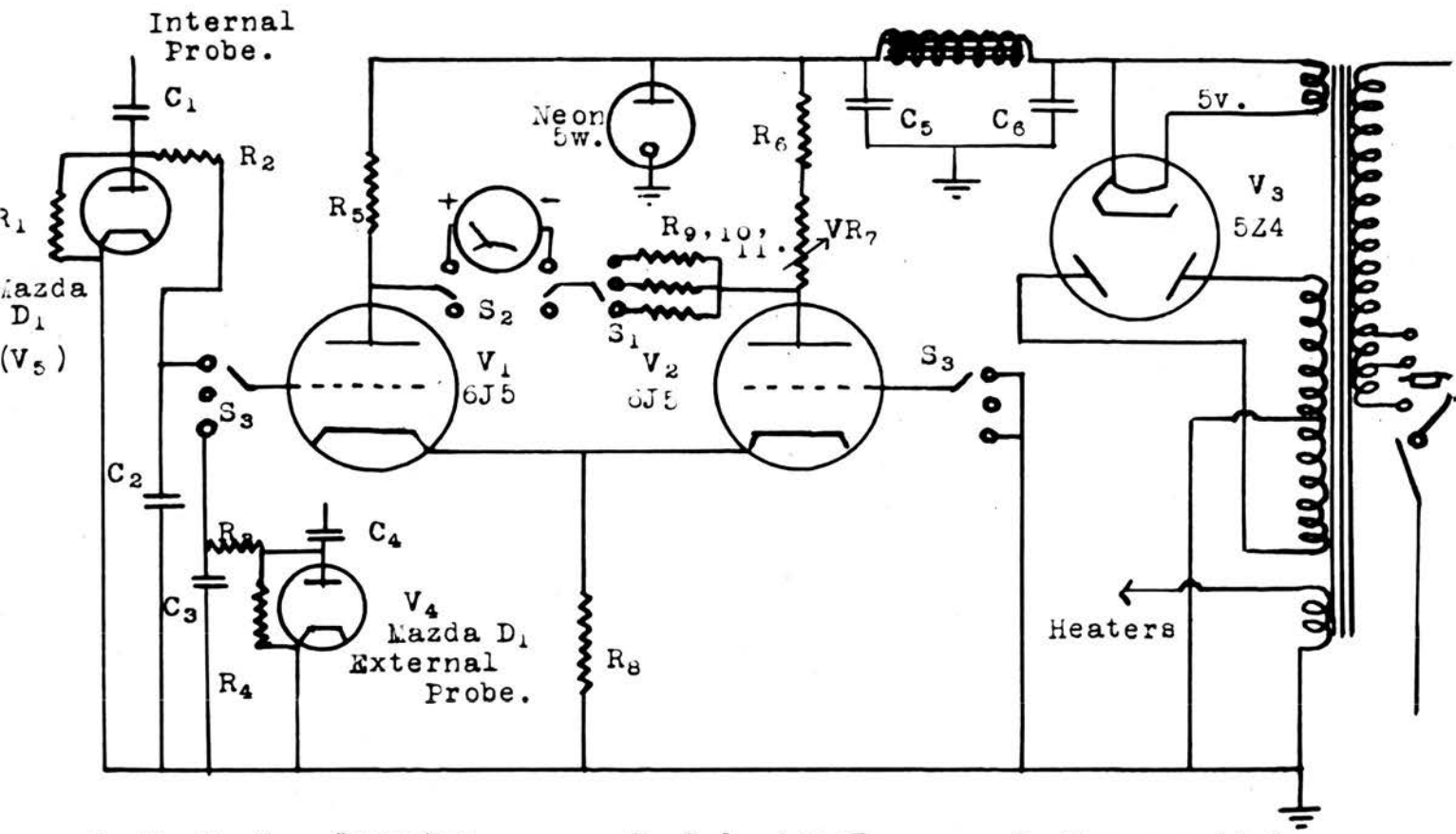
(1) Hall and Adams, J.A.C.S., 41, 1515 (1919).
(2) Jones and Bollinger, J.A.C.S., 51, 2407 (1929).
(3) Parnum, Wireless World, 51 337, 375 (1945).
(4) Astbury, J. Sci. Instr., 17, 25 (1940).
(5) Ford and Bousman, Gen. Elect. Rev., 37, 224 (1934)

Fig. 19.

The Valve Voltmeter.



R_1, R_2, R_3, R_4. 8megohms.
R_5, R_6. 10,000 ohms.
VR_7 25,000 ohms.
R_8. 400 ohms.
R_9, R_{10}, R_{11} - depend on valves .

C_1 0.1 microF.
C_2 0.01 microF.
C_3 100 pF.
C_4 100 pF.
C_5, C_6 8 microF.

S_1 Range switch.
S_2 Int./Ext. meter switc
S_3 L.F./D.C./H.F. switch

oscillations. At these times, the adaptability of the instrument for this purpose, was an advantage.

Examination of the design of the circuit, Fig.19, shows that essentially V_1 and V_2 are in opposite arms of a Wheatstone direct-current bridge. The anode resistors, R_6 and R_7, together with the zero-setting resistor VR_7, form the remaining two arms. Bias is obtained for both valves by the voltage drop in the common cathode resistor R_8. The meter (f.s.d. 1 ma.) may be zeroed by adjustment of VR until the anode potentials of V_1 and V_2 are identical. After a preliminary warming-up period, the meter zero remains steady, since changes in supply voltage, which are minimised by the voltage stabilising neon tube, cause practically identical changes in the anode potentials of V_1 and V_2. Range-switching is effected by changing the meter series resistor. The alternative ranges are, a "safety" range, a 5 volts range and a 1 volt (approx.) range; either alternating potential (with diodes in use) or steady potential.

A switch enables the internal meter to be disconnected, permitting an external indicating instrument of higher or lower sensitivity to be employed.

For low-frequency work (function switch in position 1) an internal diode, V_5, is connected in the grid circuit of V_1. Rectification of the voltage

by the diode results in a potential drop across the high load-resistor R_1 and this potential is applied to the grid of V_1 via a filter composed of R_2 and C_2. The increase in negative bias on V decreases the anode current and the anode potential rises, producing a deflection on the milliammeter.

For high-frequencies, (position 3 of the function switch) an external diode V_4 replaces V_5.

Steady potentials can be measured by direct connection to the grid circuits of either V_1 or V_2, the function switch being in position 2.

Resetting of zero is necessary if the function switch is altered because of minute "standing" currents in the diode load resistors. This phenomenon has been mentioned already in connection with the high-frequency apparatus.

Basically equivalent circuits to the present one have been previously described,[1][2][3] but the various circuits differ widely in detail.

Performance of the Low-frequency Equipment. Most investigators of low-frequency conductivity have their preferred methods and equipment but from the experience gained by prolonged use of the instruments described above, the author considers that their performance leaves little to be desired. The limit

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(1) Turner and Macnamara, Proc. Inst. Rad. Engineers, 18, 1743 (1930).
(2) Leward, Wireless World, 50, 162 (1944).
(3) Hartshorn, "Radio-frequency Measurements by Bridge and Resonance Methods", 4th Imp. 90 (1947)

to higher accuracy is not imposed by them but by the accuracy of the resistance box.

The balance-point determination is visual and though detection of the balance-point is extremely sensitive, no damage at all can be caused, however far one may be from the minimum. The present method is the equal, at least, of that employing a cathode-ray tube[1] and has the advantage of lower initial cost.

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(1) Jones and Prendergast, J.A.C.S., 62, 2919 (1940)

Subsequent Modifications.

In an effort to improve the performance and ease of operation of the equipment previously described, certain modifications were carried out.

A thermistor (Standard Telephones and Cables, Type F2311/300) was substituted in the very late stages of this work for the former wound with copper wire, whose resistance variation controlled the air thermostat (p.23). These thermistors have a very much greater temperature coefficient of resistance than metals and their small size makes response to temperature changes extremely rapid. The use of the thermistor very greatly reduced a tendency for the thermostat temperature to rise when frequent opening of the thermostat door took place during measurements owing to the influx of a cold layer of air which affected the controlling copper coil.

Frequent interchanging of the high-frequency coils eventually resulted in the base connections becoming opened out and faulty connection being obtained (p.40). Spade connections on the coils and screw terminals on the resonant circuit assembly were eventually substituted. A connecting wire passing through the metalwork of this assembly was secured rigidly in an insulating bush instead of lying loosely in a rubber grommet. Connections to the conductivity

cell were made by screw clips in place of the spring clips described on page 46.

An improvement in the performance of the high-tension voltage supply system was obtained by the substitution of a stabilising tube American Type VR105/30 for the neon lamp (p.48). Resistance R_1, Fig.13, was reduced to 40,000 ohms.

It was found possible to increase the grid resistors R_1 and R_2 (Fig.6a, p.35) to 20,000 ohms without the oscillator being subject to "squegging."

In consequence of a somewhat greater high-tension voltage being applied to the oscillator, the high tension indicating galvanometer shunt ratio was increased and galvanometer zero made independently determinable by a separate switch. This was found necessary despite the statement on p.51 owing to a periodic variation in the zero caused by a thermal e.m.f.

To reduce non-linearities in the current/deflection relationship of the resonant circuit galvanometer a scale, of radius of curvature 1 metre, replaced the straight scale employed previously (Fig.14). This had the additional advantage of maintaining the spot more accurately in focus at all deflections.

Fig. 20

Thermostat

High-frequency
Oscillator.

Controller

Bridge

Valve

Voltmeter

Amplifier

[redacted]-frequency
Oscillator

Experimental Procedure.

Low-frequency Measurements. For these measurements, solutions were made up at room temperature in graduated Pyrex flasks, previously calibrated by weight. The volumes of these solutions were corrected to 25 deg.C., on the assumptions that the temperature-coefficient of expansion of the solution was that of the solvent and the expansion of the flask was negligible for the small range considered.

When measurements were contemplated, the thermostat was switched on for at least three hours previously. The conductivity cell, in position as shown in Fig.12, was rinsed several times with the solution and then filled to the reference mark on the levelling tube. The beat-frequency oscillator, set to zero output, the amplifier and the valve voltmeter, set to "safety," were switched on and, before measurements were attempted, the bridge unity-ratio position was checked. Equal resistances were put in opposite arms of the bridge, the B.F.O. output control turned up and the bridge control knob adjusted for an approximate balance, shown by a decrease in the valve voltmeter reading. At this stage, the balancing capacitor C_1, (Fig.16) adjusted for minimum capacitance, was connected across each resistance box in turn, a large crocodile connecting-clip facilitating this

procedure. Where a slight drop was observed in the valve voltmeter reading, the clip was firmly attached, and the capacitance increased until an approximate capacitance balance was obtained. Bridge balancing was completed by switching the valve voltmeter to a more sensitive scale and readjusting bridge control and capacitor successively until a sharp minimum in the valve voltmeter reading was achieved.

With the B.F.O. volume control at its minimum and the valve voltmeter switched to "safety," the resistance boxes and balancing capacitor were interchanged. On returning the volume control and valve voltmeter range-switch to their previous positions, the bridge balance-point setting should be identical. Any departure from the previous position must have been due to slight inequalities in the resistance boxes. The bridge should then be set to a mean of the readings already determined.

If the conductivity cell replaced one of the resistance boxes, a standard box being in the opposite arm, at balance, the cell resistance equalled the box resistance, when capacitance balance also had been found. The cell resistance was periodically determined in this manner until, after a period of about two hours by which time it had attained the temperature of the thermostat, its value was constant.

Cell Constants. The cell constant of cell (1) (Fig. 10) was determined by means of 0·1 and 0·01 "demal" solutions of potassium chloride. These solutions contained 7·4789 gms. and 0·7463 gms. of potassium chloride in 1000 gms. of water. Moderately good conductivity water, specific resistance about 0·5 megohm was employed, the water being added to the potassium chloride in a weighed, clean and dry, 1 litre flask. The values of Jones and Bradshaw[1] of 0·012856(0) and 0·0014087(7) mhos for the specific conductivities of these solutions were adopted in preference to the earlier figures of Parker and Parker.[2] The specific conductivity of the calibrating solutions was corrected for the specific conductivity of the water employed.

To maintain high accuracy, the cell constants of cells (2) and (3) were determined from that of cell (1) by measuring the cell resistances with the same weak potassium chloride solution of arbitrary concentration. A further check for cell (3) was provided by the duplication of results using the same solution of 0·01 M sodium dodecyl sulphate.

High-frequency Measurements. At high frequencies, one is compelled to modify procedure. Results must

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(1) Jones and Bradshaw, J.A.C.S., 55, 1780 (1933).
(2) Parker and Parker, J.A.C.S., 46, 312 (1924).

be relatively more rapidly obtained if accuracy is not to suffer from slow changes which, while immaterial over periods of about an hour, affect observed deflections over much longer periods. It is advisable, therefore, to have all solutions at the correct temperature before measurements commence and confine manipulation to within the thermostat.

Two potassium chloride solutions, whose low-frequency resistances differed by about 3% and another solution whose high-frequency resistance was to be determined (the "unknown") were brought to 25°C. quickly in a small water thermostat which was also employed to adjust volumes so that molarities of colloidal electrolyte solutions were correct at this temperature. The corrections noted above in the low-frequency case were thus rendered unnecessary.

All three solutions were transferred to the air thermostat and left for a further three hour period. In the meantime, all low-frequency and high-frequency equipment was switched on with the exception of the high-tension supply to the oscillator. This period allowed the oscillator low-tension supply in particular to become steady and was very desirable if these accumulators had been freshly charged.

About half an hour previous to measurements being taken the high tension voltage was applied to the

oscillator with the requisite coil plugged in. The voltage itself was adjusted to give a standard deflection on its indicating galvanometer, attention being paid to the galvanometer zero setting. At the end of a further 10 minutes, during which time the oscillator components had reached operating temperature, and the frequency had become very stable, the oscillator was accurately tuned to the desired frequency. The conductivity cell, connected across the resonant circuit equipped with the correct coil was washed two or three times with one of the potassium chloride solutions, and then filled to its reference level. At first by means of the coarse, and later by means of the fine tuning capacitors, the resonant circuit was adjusted to attain peak deflection of the resonant circuit indicating galvanometer. A deflection of about 60 scale divisions was generally employed. If the deflection was smaller than this, coupling between oscillator and resonant circuit was increased by moving the oscillator down the guide-rails on the thermostat wall. If the deflection was too large the reverse procedure was adopted. Occasionally, when the deflection was still too great to be reduced by the permissible traverse of the oscillator, an aluminium plate with a large hole in its centre was inserted between oscillator and resonant circuit. Since the proximity of this plate to the

oscillator coil slightly affected the frequency generated, frequency rechecking was advisable. In all cases the oscillator was securely clamped in its new position. When the high tension voltage had been ascertained correct, the resonant circuit galvanometer deflection was read, the oscillator switched off and the galvanometer zero found. The original deflection was generally restored when the oscillator was switched on again. This question is dealt with later.

On completing the procedure described above, the conductivity cell, disconnected from the resonant circuit, was reconnected to the low-frequency conductivity bridge and the cell resistance at low frequencies determined. Replacement of the resonant circuit connecting leads should again reproduce the original deflection. With at least two rinsings, another solution, this time the "unknown," was substituted in the conductivity cell. The deflection and low-frequency resistance were determined as before, the resonant condition being adjusted by the fine tuning capacitor, if necessary, to compensate for the dielectric constant of the fresh solution, if different from that of the calibrating solution. A further experiment with the remaining potassium chloride solution completed the set of measurements.

Calculation of Results. From the two deflections measured with the potassium chloride solutions and their corresponding resistances, the gradient of the deflection versus resistance curve can be ascertained. Knowing the deflection obtainable with the solution of unknown high-frequency resistance, its resistance value at high frequency can be found. The accuracy of this method depends on the validity of the assumption of a linear relationship between deflection and resistance over the small range considered and this assumption will be considered later.

If Λ_ω and Λ_0 are the equivalent conductivities of the unknown solution at angular frequencies ω and zero (the latter assumed identical with the low-frequency conductivity value), the required fraction is $100\ \frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$. On the erroneous assumption that the observed deflection for the unknown solution gives a high-frequency resistance (R_ω) for that solution equal to the low-frequency resistance (R_0^{KCl}) of the potassium chloride solution for the same deflection, we can equate this fraction to $100\ \frac{R_0 - R_\omega^{(1)}}{R_\omega}$, R_0 being the low-frequency resistance with the "unknown" solution in the cell. Now, since the high-frequency

(1) Schmid and Erkkila, Z.f.Elektrochem., 42, 740 (1936).

resistances of the potassium chloride solutions are not identical with their low-frequency values, it is necessary to correct theoretically for the increase in conductivity of the potassium chloride solution at the concentration and frequency in question.(1)

Theoretical Basis for the Calculation. If Λ_ω and Λ_o are the equivalent conductivities of a given solution at high and low frequencies respectively, the required "high-frequency effect" as a percentage is $100\ \frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$. Since $\Lambda_\omega = K_\omega v$ and $\Lambda_o = K_o v$, where K_ω and K_o are the specific conductivities of the solution at high and low frequencies and v is the volume in c.c. containing a gram equivalent of the electrolyte, the "high-frequency effect" equals $100\ \frac{K_\omega - K_o}{K_o}$ (v cancels). Further, if $K_\omega = \frac{C_\omega}{R_\omega}$ and $K_o = \frac{C_o}{R_o}$ where C_ω and C_o are the apparent cell constants at high and low frequencies, we can write $100\ \frac{K_\omega - K_o}{K_o}$ equal to

$$100\ \frac{\frac{C_\omega}{R_\omega} - \frac{C_o}{R_o}}{\frac{C_o}{R_o}}$$

With change in frequency, the capacitative part of the cell impedance is experimentally compensated (by retuning to resonance) and, since the cell constant is independent of the resistive part, C_ω can be put equal to C_o. The required "high-frequency effect" becomes

(1) Falkenhagen, "Electrolytes," 228.

equal to $100\ \frac{R_o - R_\omega}{R_\omega}$ as found by Schmid and Erkkila, (loc.cit.).

The Potassium Chloride Correction. It has been mentioned already that the high-frequency resistance of the unknown solution (R_ω) has been taken equal to the low-frequency resistance of the potassium chloride solution (R_o^{KCl}). Owing to the significant dispersion of the conductivity of potassium chloride solutions, this when substituted in the expression $\frac{R_o - R_\omega}{R_\omega}$ (the factor of 100 being omitted for convenience) gives the apparent "high-frequency effect" equal to $\frac{R_o - R_o^{KCl}}{R_o^{KCl}}$ In fact, the measured high-frequency deflection for potassium chloride depends on its high-frequency resistance R_ω^{KCl}. The true "high-frequency effect" is thus $\frac{R_o - R_\omega^{KCl}}{R_\omega^{KCl}}$. The difference between true and apparent effects is the correction to be applied.

$$\text{i.e. } \frac{R_o - R_\omega^{KCl}}{R_\omega^{KCl}} - \frac{R_o - R_o^{KCl}}{R_o^{KCl}} = \frac{R_o}{R_\omega^{KCl}} - \frac{R_o}{R_o^{KCl}}$$

$$= \frac{R_o}{R_o^{KCl}}\left[\frac{R_o^{KCl} - R_\omega^{KCl}}{R_\omega^{KCl}}\right]$$

This correction is, in any case, small (a maximum of 0·4% over the frequency range considered) and, since R_o in no case differs from R_o^{KCl} by more than about 15%, the correction is approximately equal to

$\frac{R_0^{KCl} - R_\omega^{KCl}}{R_\omega^{KCl}}$, which can readily be shown to equal

$\frac{\Lambda_\omega^{KCl} - \Lambda_0^{KCl}}{\Lambda_0^{KCl}}$

Calculation of the Correction. For the corrections at 25°C., the equivalent conductivity of potassium chloride[1] is plotted against concentration at this temperature. Taking an average resistance value for a given set of results, an average concentration can be determined fairly accurately by two successive approximations (since the resistance of a solution in a cell is dependent on the concentration and this affects the calculation of the equivalent conductivity also, though to a small extent in the case of potassium chloride). The relaxation time, θ, can be found from the formula[2] $\theta = \frac{8{\cdot}85 \times 10^{-11}}{\gamma^* \Lambda_\infty^*} D_0$ where D_0 is the dielectric constant of the solvent, γ^* is the concentration in equivalents per litre and Λ_∞^* is the equivalent conductivity of the potassium chloride at infinite dilution, all at the temperature concerned. For the various frequencies under consideration, the product $\omega\theta$ can be ascertained. From Table 31 (Falkenhagen, loc.cit.) a graph of $\omega\theta$ against $\frac{\Lambda_{1\omega}}{\Lambda_{10}}$, where $\Lambda_{1\omega}$ and Λ_{10} are the contributions of the "relaxation" effect to the lowering of the equivalent conductivity at frequencies ω and zero, enables this ratio to be

(1) International Critical Tables, 6, 234.
(2) Falkenhagen, "Electrolytes," 213.

determined at the frequencies in question. Multiplication of $(1 - \frac{\Lambda_{1\omega}}{\Lambda_{10}})$ by Λ_{10} [1] gives the actual increase in conductivity $\Lambda_{10} - \Lambda_{1\omega}$. Division of this value by Λ_0, the equivalent conductivity at low frequency and subsequent multiplication by 100 gives the required correction.

The calculation of the correction for the results at 35°C. was made more difficult by the absence of conductivity data for potassium chloride at this temperature. Values were obtained graphically from the conductivity data at various temperatures.[2] An infinite dilution equivalent conductivity value of 178·3 mhos was also obtained in this way. The dielectric constant of water at this temperature was calculated[3] as 74.

At 25°C. the dielectric constant value of 78·8 for water and infinite dilution equivalent conductivity value for potassium chloride of 149·8 mhos as given by Falkenhagen, were employed in calculating the corrections.

Discussion of the Method. The accuracy of the method depends on the validity of the assumption that the relationship between cell resistance and galvanometer

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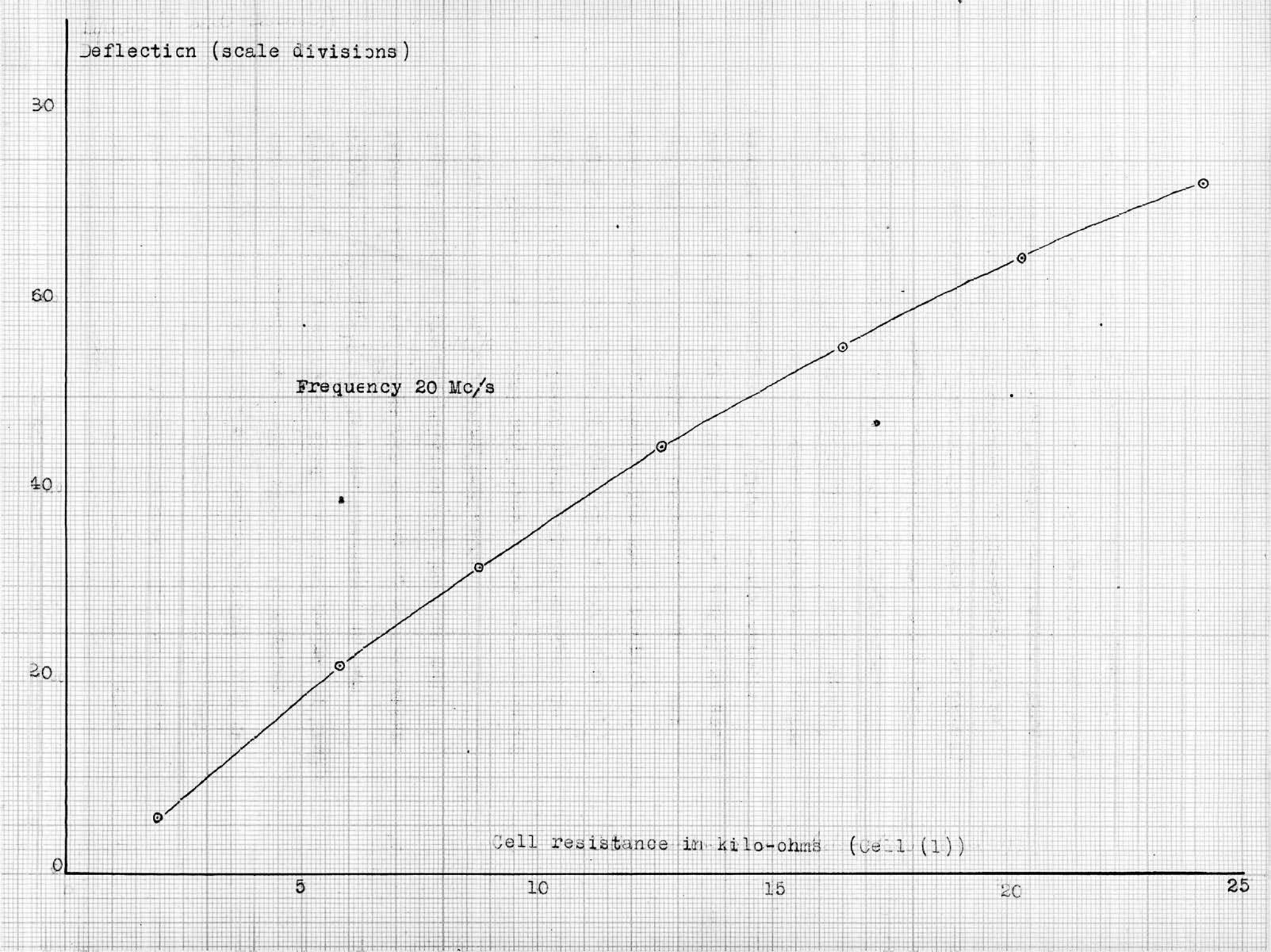
(1) Falkenhagen, equation (533), 212.
(2) International Critical Tables, 6, 234.
(3) International Critical Tables, 6, 78.

Fig. 21.


Deflection (scale divisions)
30
60
40
20
0
Frequency 20 Mc/s
Cell resistance in kilo-ohms (Cell (1))
5
10
15
20
25

deflection is linear. If this were strictly true, the resonant circuit losses, without the cell connected would require to be zero. Inevitably, small losses exist in the coil and its connections and in the tuning capacitors. The circuit is further damped by the rectifying diode and its resistive load. Strict proportionality is also dependent on the linearities of the diode and measuring galvanometer. Fig.21 shows a typical relationship between cell resistance and galvanometer deflection.

Under experimental conditions, the influence of all the factors mentioned above may be reduced to negligible proportions by employing a sufficiently small deflection range over which the linearity of deflection and resistance is extremely high. For instance, deflections of 69·15, 70·62 and 71·69 scale divisions were obtained at 70Mc/s, where circuit losses should be high for cell resistances of 10,749, 11,024 and 11,235 ohms respectively. When these values are plotted, they lie in a straight line. Normally, a much smaller deflection and resistance range is employed. Further diminution of the effect of non-linearities is achieved by arranging, as is aimed at under actual experimental conditions, that one of the calibrating solution deflections lies very close to that of the "unknown" solution. The

constancy of the slope of the deflection versus resistance relationship, for similar values of resistance and deflection, over the entire frequency range is an indication of the independence of the results of the measuring circuit.

An apparent dependence of the "high-frequency effect" on frequency at a given concentration was originally found and thought, at the time, to have some physico-chemical significance. Simultaneous fluctuations in the tuning capacitor settings for resonance were observed. Eventually, after a considerable number of results had been obtained, the cause of these effects was traced to over-coupling between oscillator and resonant circuits resulting in ambiguity in the resonant circuit tuning. A cure was accomplished by greatly increasing the power from the oscillator by a substantial increase in its high-tension voltage and correspondingly diminishing the coupling between oscillator and resonant circuit. Unfortunately, with the increased voltage, a small drift in oscillator output was noticeable on re-applying the voltage. Normally, the deflection returned to its former setting but occasionally a distinct shift was observed. It was, therefore, considered advisable, when the high-tension supply was interrupted, to ascertain that the deflection attained its former

value. Heating of the oscillator valve electrodes, especially the grids, was thought to be responsible for the effect.

Objection to the method might be raised on the grounds that the temperature of the solution in the cell might be different from that in the thermostat owing to the application of the high-frequency voltage. Power dissipation in the cell is, in fact, very small even under the worst conditions and is estimated at about 5 mW (about 5 volts RMS across a resistance of 5000 ohms). The total input power from the high-tension source is only about three watts and total oscillator output probably about one and a half watts. Only a very small fraction of this is actually dissipated in the electrolyte. Moreover, the potassium chloride calibrating solution would be affected in a similar manner and its resistance would drift in the same direction. In practice, no resistance drift attributable to this cause was ever observed.

Temperature drift was noted when frequent opening of the thermostat doors took place during a succession of experiments. This had its origin in the over-compensation of the thermostatic controlling device and the problem was eventually solved by fitting a thermistor as described under "Modifications."

The leads to the conductivity cell were purposely kept very short to minimise their inductance and their thermal conductivity might be sufficient to give some slight temperature disturbing effect.[1]

It has been mentioned that retuning of the resonant circuit was generally necessary on replacing the potassium chloride solution by that of the colloidal electrolyte owing to the difference in dielectric constants of the two solutions. The difference in tuning capacitor settings was, however, too small to give any accurate or useful information.

Compared with the apparatus used by Schmid and Erkkila[2] the existence of a separate tuned circuit may be considered an unnecessary complication in an apparatus already requiring so much manipulation. The separate tuned circuit has the advantages of freeing the oscillator from the effects of the conductivity cell and of rejecting very effectively harmonics, which may give inaccurate results and which are inevitably present in the oscillator output.

Estimated Accuracy. The accuracy of the results is dependent on a large number of factors whose individual contribution to error would be very difficult to evaluate. In general, by comparison with the errors

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(1) Davies, "The Conductivity of Solutions," 2nd Ed., 43 (1933).
(2) Schmid and Erkkila, Z.f.Elektrochem., 42, 737 (1936)

in the measurement of the high-frequency deflection, all errors in low-frequency resistance measurement may be neglected.

With cell (1) reproducibility and the consistency of results at different frequencies indicated that precision was of the order of $\pm$ 0·2%. The results with cell (2) at 35°C. were not so consistent but, for the remaining results at 25°C. with this cell, precision was about $\pm$ 0·4% or somewhat better. To some extent, the results were dependent on the actual resistance range and the frequencies employed. Generally, at the higher frequencies precision deteriorates. In these cases where the high-frequency effect rose steeply with frequency, the accuracy of the frequency generated assumed some importance but the method of calibration and frequency standard employed ensured that error from this cause was not a determining factor. Small temperature variations, while affecting the absolute resistance value in any given experiment do not seem to affect the high-frequency effect to any noticeable degree.

There seems no direct way of checking the absolute accuracy of these experiments but this is probably of the same order as the precision.

Where duplicate experiments were carried out, these have been given in the following tables of results.

The following typical result illustrates the information noted and the method of calculation employed.

Frequency 60·0 Mc/s. Oscillator tuning 70·4.

	Solution	Low-frequency Resistance (ohms)	Resonant Circuit Setting	High-frequency Deflection	Galvo. Zero	Total Deflection
(1)	Potassium Chloride	8341	86·2	77·11	13·82	63·29
(2)	0·025 M sodium dodecyl sulphate	8885	83·5	75·73	13·76	61·97
(3)	Potassium Chloride	8144	86·8	75·81	13·78	62·03

From (1) and (2) we obtain the gradient of the deflection and resistance relationship, i.e. 1·26 scale divisions correspond to 197 ohms. The deflection difference between (2) and (3), 0·06 scale divisions, thus corresponds to 10 ohms. In this particular instance, this must be subtracted from (3) to give the apparent high-frequency resistance, 8134 ohms. The apparent high-frequency effect is thus $100 \cdot \frac{8885 - 8134}{8134}$ = 9·23%. The potassium chloride correction at 60 Mc/s is 0·29% so that the true high-frequency effect is 9·52%.

Low-frequency Results.

Table I.

Sodium Dodecyl Sulphate at 25 deg.C. (at 1000 c/s).

Concentration in moles per litre, corrected to 25 deg.C.	Cell Constant	Cell resistance (in ohms)	Corrected Specific Conductivity.	Equivalent Conductivity.
0·099755	8·7055	2889·0	0·0030113	30·18(7)
0·089856	8·7055	3202	0·0027168	30·23(5)
0·079904	8·7055	3570	0·0024365	30·49(3)
0·069874	8·7055	4035	0·0021555	30·84(9)
0·059892	8·7055	4611	0·0018860	31·49(0)
0·049877	8·7055	5377	0·0016170	32·42(0)
0·042423	8·7055	6133	0·0014175	33·41(3)
0·035000	8·7055	7115	0·0012214	34·89(9)
0·029964	8·7055	7944	0·0010939	36·50(6)
0·024960	8·7055	9005	0·00096480	38·65(4)
0·022464	8·7055	9586	0·00090620	40·34(0)
0·019968	8·7055	10323	0·00084137	42·13(6)
0·017472	8·7055	11125	0·00078037	44·67(6)
0·014976	0·61945	863·6	0·00071634	47·83(3)
0·012485	0·61945	946·7	0·00065237	52·25(2)
0·011236	0·61945	977·0	0·00063208	56·25(3)
0·0099880	8·7055	14407	0·00060231	60·30(3)
0·0099880	0·61945	1025·0	0·00060239	60·31(2)

49

Table I. (cont.).

Sodium Dodecyl Sulphate at 25 deg.C. (at 1000 c/s).

Concentration in moles per litre, corrected to 25 deg.C.	Cell Constant	Cell resistance (in ohms)	Corrected Specific Conductivity.	Equivalent Conductivity.
0·0089838	0·61945	1071·4	0·00057621	64·13(9)
0·0084847	0·61945	1104·0	0·00055914	65·90(0)
0·0079856	0·61945	1150·0	0·00053670	67·20(9)
0·0074940	0·61945	1220·3	0·00050567	67·47(7)
0·0049920	0·61945	1797·5	0·00034267	68·66(0)
0·0024955	0·61945	3499·0	0·00017509	70·16(3)
0·00124775	0·61945	6790	0·00008928	71·55(3)

High-frequency Results.

Table II.

0·005M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$
18·0	40	25,055	0·16	0·15	0·31
25·0	25	25,470	0·10	0·20	0·30
30·0	-15	25,465	-0·05	0·22	0·17
(40·0	85	25,175	0·34	0·28	0·62
(40·0	108	25,320	0·43	0·28	0·71
50·0	125	25,200	0·50	0·32	0·82
60·0	140	25,110	0·56	0·35	0·91
(70·0	190	25,050	0·76	0·37	1·13
(70·0	197	24,988	0·79	0·37	1·16

Corrections based on average resistance = 25,000 ohms.

" concentration = 0·0024M

" equivalent conductivity = 145·9 mhos.

Table III.

0·008M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
8·75	32	16,132	0·20	0·04	0·24
15·0	50	16,151	0·31	0·08	0·39
20·0	51	16,179	0·31	0·13	0·44
25·0	67	16,037	0·42	0·16	0·58
30·0	89	16,074	0·55	0·20	0·75
40·0	124	16,071	0·77	0·25	1·02
40·0	118	15,760	0·75	0·25	1·00
40·0	80	16,055	0·50	0·25	0·75
50·0	100	15,973	0·63	0·30	0·93
60·0	140	16,050	0·87	0·35	1·22
60·0	122	16,048	0·76	0·35	1·11
70·0	194	15,989	1·21	0·38	1·59

Corrections based on average resistance = 16,075 ohms.

" concentration = 0·00374M

" equivalent conductivity = 144·8 mhos.

Table IV.

0·01M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
10·0	71	14,341	0·50	0·04	0·54
15·0	107	14,278	0·75	0·08	0·83
(20·0	111	14,363	0·77	0·11	0·88
(					
(20·0	98	14,225	0·69	0·11	0·80
(25·0	179	14,196	1·26	0·15	1·41
(					
(25·0	135	14,385	0·94	0·15	1·09
30·0	198	14,200	1·39	0·19	1·58
35·0	214	14,202	1·51	0·22	1·73
40·0	235	14,198	1·66	0·24	1·90
(45·0	295	14,107	2·04	0·27	2·31
(					
(45·0	258	14,187	1·82	0·27	2·09
51·0	332	14,100	2·36	0·30	2·66
56·0	386	13,762	2·80	0·32	3·12
60·0	382	13,865	2·76	0·33	3·09
63·0	410	13,925	2·95	0·35	3·30
66·0	444	13,868	3·20	0·36	3·56
70·0	483	13,817	3·49	0·37	3·86

Corrections based on average resistance = 14,150 ohms.

average concentration = 0.00425M

" equivalent conductivity = 144.4 mhos.

Table V.

0·015M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
10·0	46	11,773	0·39	0·03	0·42
15·0	60	11,785	0·51	0·06	0·57
20·0	141	11,802	1·20	0·09	1·29
25·0	205	11,674	1·76	0·13	1·89
30·0	277	11,625	2·38	0·16	2·54
35·0	349	11,641	3·00	0·19	3·19
40·0	427	11,510	3·71	0·22	3·93
45·0	481	11,433	4·21	0·25	4·46
50·0	549	11,383	4·83	0·27	5·10
56·0	639	11,312	5·65	0·30	5·95
60·0	719	11,208	6·41	0·32	6·73
66·0	818	11,112	7·36	0·34	7·70
(70·0	902	11,090	8·14	0·36	8·50
(70·0	871	11,084	7·86	0·36	8·22

Corrections based on average resistance = 11,450 ohms.
" concentration = 0.0053M
" equivalent conductivity = 143.3 mhos.

Table VI.

0·025M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
10.0	4	8842	0·05	0·02	0·07
15·0	49	8756	0·56	0·04	0·60
20·0	104	8820	1·24	0·07	1·31
25·0	175	8692	2·01	0·09	2·10
30·0	221	8634	2·56	0·12	2·68
(35·0	294	8601	3·42	0·16	3·58
(35·0	303	8501	3·56	0·16	3·72
40·0	366	8500	4·31	0·19	4·50
45·0	451	8436	5·35	0·21	5·56
50·0	542	8277	6·55	0·24	6·79
56·0	644	8211	7·83	0·26	8·09
60·0	745	8084	9·23	0·29	9·52
63·0	807	8118	9·94	0·30	10·24
66·0	835	8029	10·40	0·32	10·72
70·0	912	7940	11·49	0·33	11·82

Corrections based on average resistance = 8,300 ohms.
" concentration = 0.00735M
" equivalent conductivity = 142.4 mhos.

Table VII

0·05M sodium dodecyl sulphate at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
10·0	0	5393	0·00	0·01	0·01
15·0	7	5378 5385	0·13	0·02	0·15
20·0	37	5362 5399	0·69	0·04	0·73
25·0	70	5323 5393	1·31	0·06	1·37
30·0	93	5276 5369	1·76	0·08	1·84
35·0	140	5229 5369	2·68	0·10	2·78
40·0	191	5199 5390	3·68	0·12	3·80
45·0	245	5118 5363	4·78	0·14	4·92
50·0	323	5067 5390	6·37	0·17	6·54
56·0	402	5015 5417	8·02	0·20	8·22
60·0	448	4911 5359	9·12	0·22	9·34
63·0	511	4845 5356	10·54	0·23	10·77
66·0	570	4784 5354	11·92	0·25	12·17
70·0	634	4784 5418	13·24	0·26	13·50

Corrections based on average resistance = 5120 ohms.
" concentration = 0.0121M
" equivalent conductivity = 140.5 mhos.

Table VIII

0·025M sodium dodecyl sulphate + 0·005M sodium chloride at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
10·0	26	5902	0·44	0·01	0·45
15·0	45	5895	0·76	0·03	0·79
20·0	83	5841	1·42	0·04	1·46
25·0	114	5860	1·95	0·07	2·02
30·0	134	5815	2·30	0·09	2·39
(35·0	164	5777	2·84	0·10	2·94
(35·0	191	5754	3·01	0·10	3·11
(40·0	213	5677	3·75	0·13	3·88
(40·0	209	5700	3·67	0·13	3·80
45·0	231	5683	4·07	0·16	4·23
50·0	265	5662	4·68	0·19	4·87
54·0	306	5654	5·41	0·21	5·62
60·0	359	5583	6·43	0·23	6·66
66·0	413	5533	7·47	0·25	7·72
70·0	437	5484	7·97	0·27	8·24

Corrections based on average resistance =5700 ohms.
" concentration =0.0108M
" equivalent conductivity =141·0 mhos.

Table IX

0·001M sodium hexadecyl sulphate at 35°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
3·5	265	18,475	1·43	0·02	1·45
5·0	500	18,055	2·77	0·03	2·80
9·0	825	17,885	4·61	0·04	4·65
20·0	1,293	17,047	7·59	0·06	7·65
30·0	1,692	16,928	10·01	0·07	10·08
40·0	2,019	16,541	12·20	0·07	12·27
50·0	2,255	16,295	13·83	0·08	13·91
56·0	2,375	16,205	14·66	0·08	14·74

Corrections based on average resistance = 17,300 ohms.

" concentration = 0.000374M

" equivalent conductivity = 177.8 mhos

These and succeeding results were obtained with the use of cell (2) whose cell constant was 1·148.

Table X.

0·001M cetyl pyridinium chloride at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega-\Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega-\Lambda_o}{\Lambda_o}$
5·0	146	14,066	1·04	0·09	1·13
10·0	174	14,034	1·24	0·14	1·38
15·0	163	13,953	1.17	0·17	1·34
20·0	183	14,026	1·30	0·19	1·49
30·0	262	13,934	1·88	0·22	2·10
40·0	290	13,916	2·08	0·23	2·31
50·0	319	13,879	2·30	0·25	2·55

Corrections based on average resistance = 13,950 ohms.

" concentration = 0·000557M

" equivalent conductivity = 148·2.

Table XI.

0·002M cetyl pyridinium chloride at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
5·0	127	10,086	1·26	0·07	1·33
10·0	272	9,868	2·76	0·13	2·89
20·0	495	9,660	5·12	0·20	5·32
30·0	643	9,481	6·78	0·23	7·01
(40·0	793	9,275	8·54	0·25	8·79
(40·0	784	9,366	8·29	0·25	8·54
50·0	877	9,205	9·53	0·27	9·80
60·0	1000	9,061	11·03	0·29	11·32

Corrections based on average resistance = 9550 ohms.

" concentration = 0·000815M

" equivalent conductivity = 147.7 mhos.

Table XII.

0·003M cetyl pyridinium chloride at 25°C.

Frequency in Mc/s	Apparent resistance change (ohms.)	Apparent high-frequency resistance (ohms.)	Apparent $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$	Theoretical correction for potassium chloride	Corrected $100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
5·0	109	8078	1·35	0·06	1·41
10·0	235	7955	2·95	0·12	3·07
20·0	473	7724	6·12	0·20	6·32
30·0	631	7518	8·39	0·24	8·63
40·0	800	7370	10·84	0·26	11·10
(50·0	893	7264	12·29	0·29	12·58
(50·0	898	7281	12·33	0·29	12·62
60·0	1008	7176	14·02	0·31	14·33

Corrections based on average resistance = 7,630 ohms.

" concentration = 0·00102M

" equivalent conductivity = 147·4 mhos.

Discussion.

Conductivity Results at Low Frequencies. The low-frequency conductivity results for sodium dodecyl sulphate, when plotted as in Fig.37 (at end of thesis), give a smooth curve in very good agreement with the best of other data available.[1] The results of Howell and Robinson[2] are somewhat higher and these workers subsequently admitted a systematic error at concentrations less than 0·007N (Ward[3]). From a comparison of other data it is obvious that discrepancies exist over a much wider range. Their contention that Lottermoser and Püschel's results[4] were low because of a larger water correction is not supported by Ward who considers Lottermoser and Püschel's results quite accurate. As previously mentioned, the water correction has been applied to the author's results in its entirety.

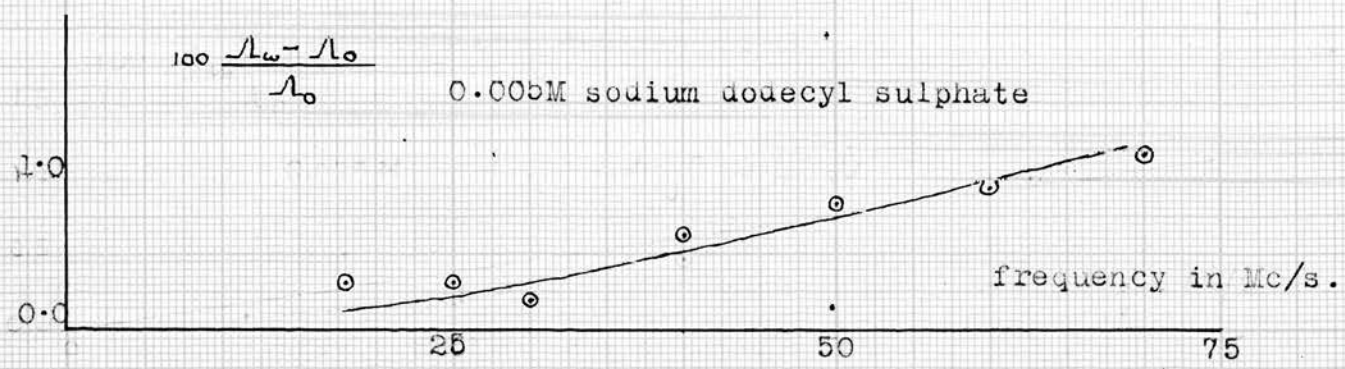
The curve (Fig.37) exhibits the characteristic features of that of a colloidal electrolyte. At low concentrations, there is a gradual decrease of equivalent conductivity with increasing concentration.

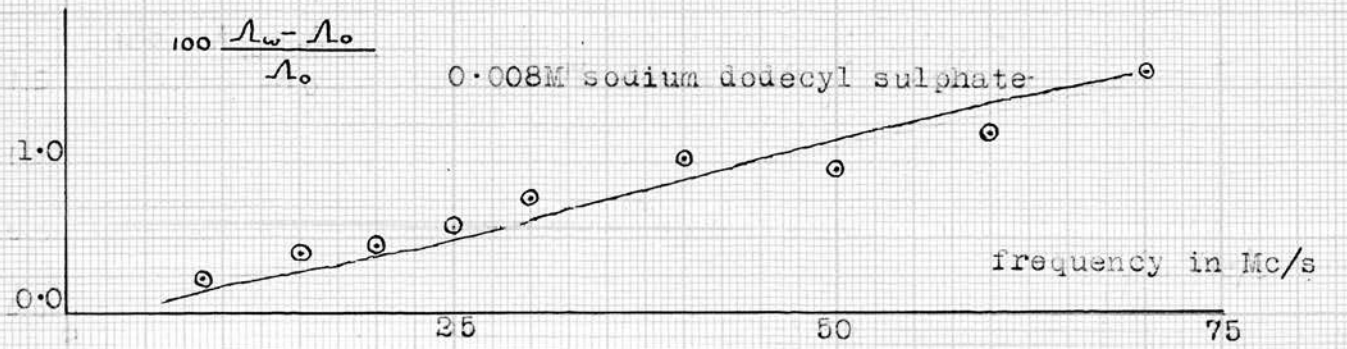
In the region of the "critical concentration" there is a sudden change of slope, the curve acquiring a steep downward trend. At still greater concentrations, the slope is reduced and eventually may be slightly reversed.[2] Very high concentrations result

in an equivalent conductivity fall with concentration increase. These last two regions have not been reached in the present curve.

For cetyl pyridinium chloride at 25°C., values of the low-frequency conductivity at the three concentrations 0·001, 0·002 and 0·003 M. can be obtained by adding the resistance change to the observed high frequency resistance. Taking average cell resistances as 14,200, 10,140 and 8220 ohms. respectively, we obtain, using the cell constant 1·148 (cell 2), equivalent conductivities 80·8, 56·6 and 46·6 mhos. respectively with no water correction applied. Comparison with Malsch and Hartley's results[5] and also those of Schmid and Larsen[6] shows that the present values are all lower. The application of a water correction and the uncertainty of the degree of hydration (see p.14) would tend to add to the discrepancies. Schmid and Larsen, who obtain higher values than Malsch and Hartley, consider their compound to be slightly impure. On this basis, the purity of the present preparation should be very high. There is some evidence to support this view. Lottermoser and Frotscher,[7] who took great care in the preparation of cetyl pyridinium chloride, unfortunately did not make measurements at 25°C. or at the concentrations specified. However, by extrapolation and interpolation it is possible to obtain

Figs. 22, 23, 24.


100 Λω − Λ0 / Λ0
0·005M sodium dodecyl sulphate
1·0
0·0
frequency in Mc/s.
25
50
75


100 Λω − Λ0 / Λ0
0·008M sodium dodecyl sulphate
1·0
0·0
frequency in Mc/s
25
50
75

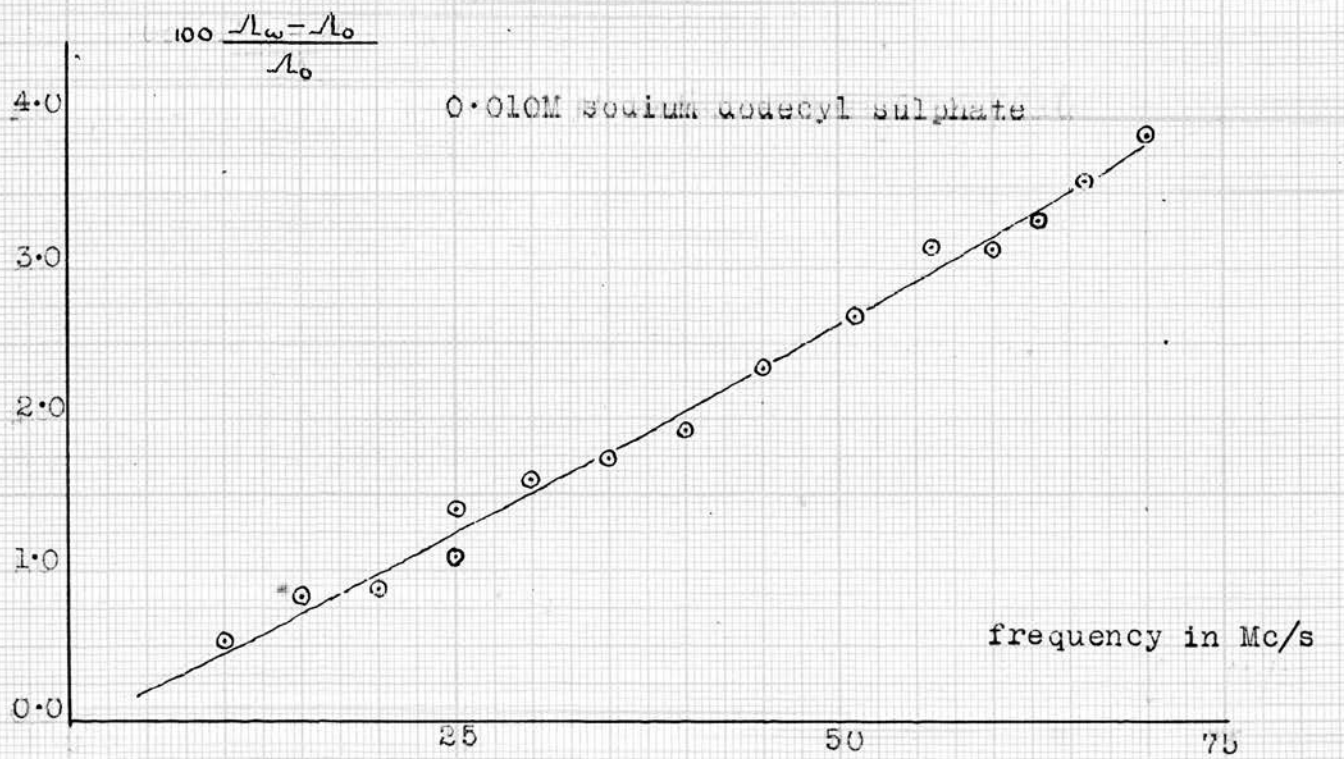

100 Λω − Λ0 / Λ0
0·010M sodium dodecyl sulphate
4·0
3·0
2·0
1·0
0·0
frequency in Mc/s
25
50
75

Fig. 25.

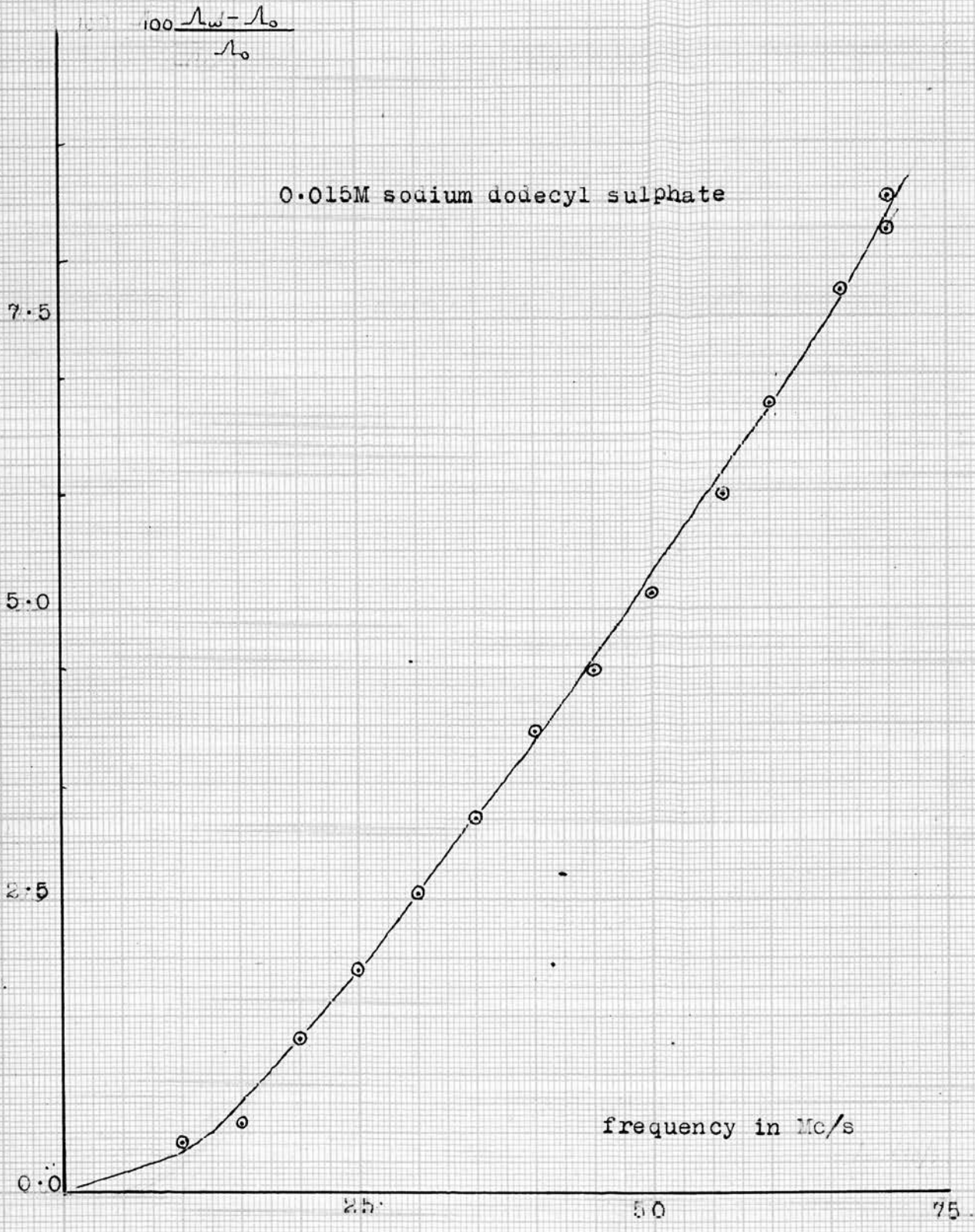

$100\frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$
0·015M sodium dodecyl sulphate
7·5
5·0
2·5
0·0
25
50
75
frequency in Mc/s

Fig. 26.

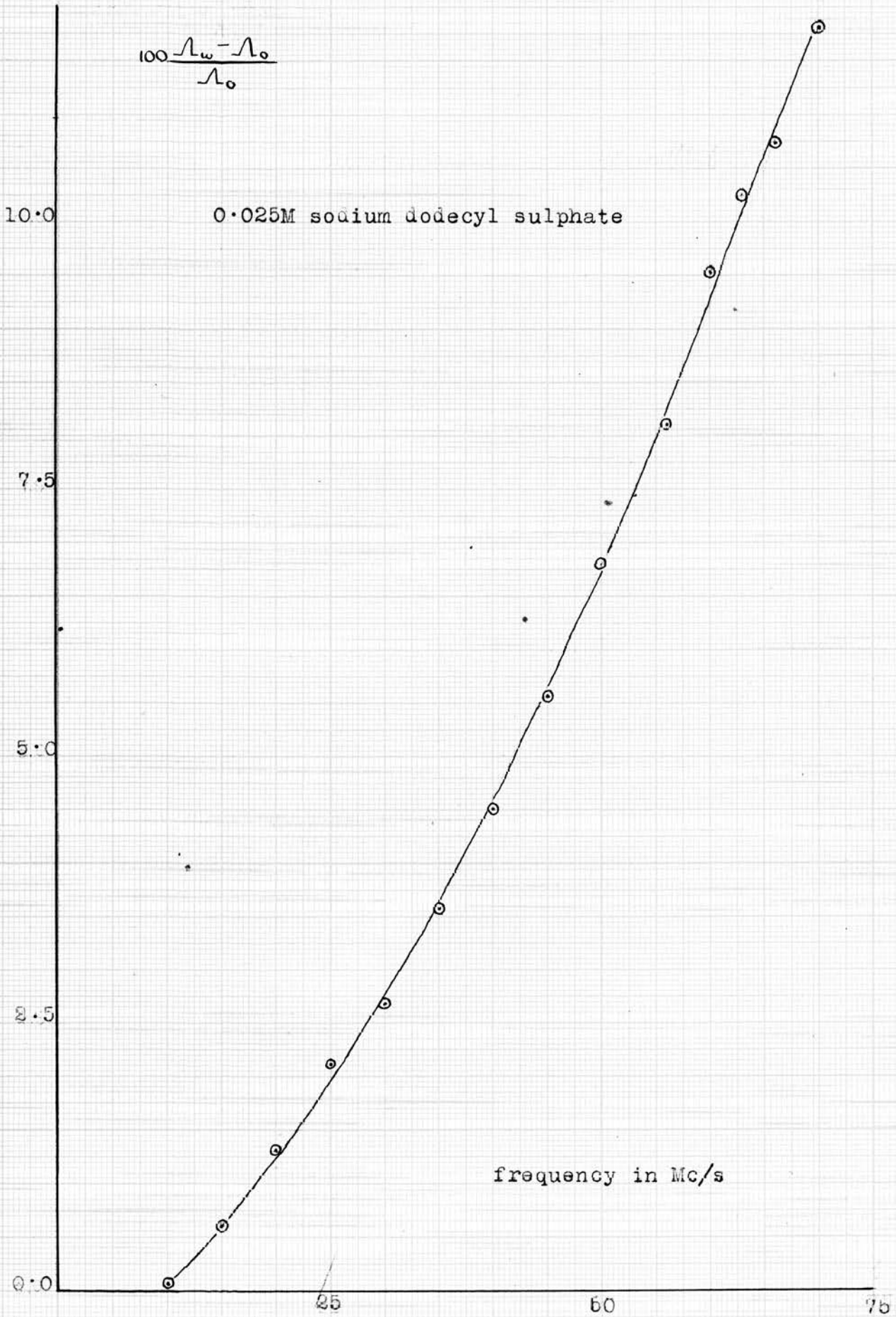
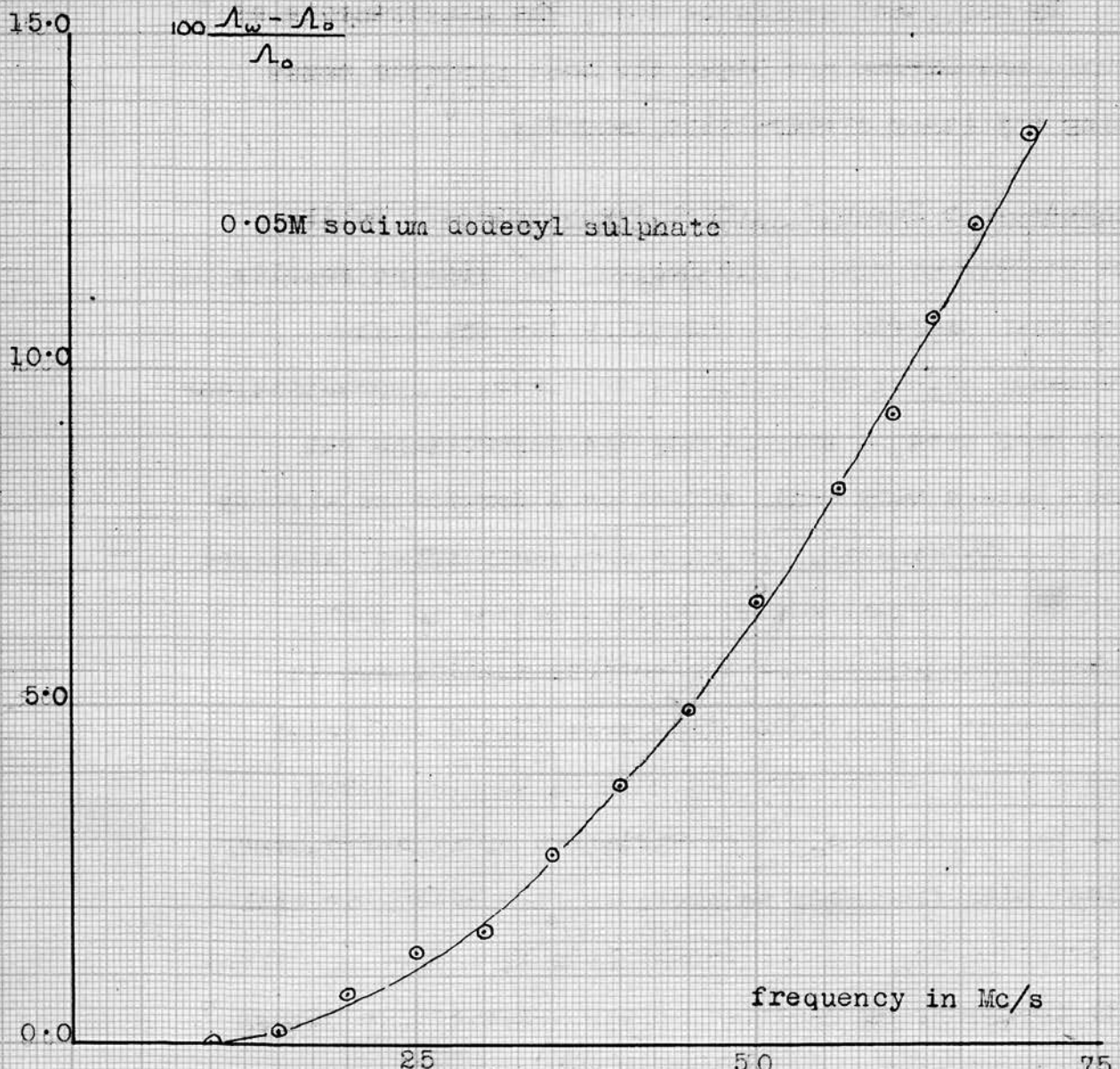

$\frac{100\Lambda_\omega - \Lambda_0}{\Lambda_0}$
0·025M sodium dodecyl sulphate
10·0
7·5
5·0
2·5
0·0
25
50
75
frequency in Mc/s

Fig. 27.


15·0
$100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
0·05M sodium dodecyl sulphate
10·0
5·0
0·0
frequency in Mc/s
25
50
75

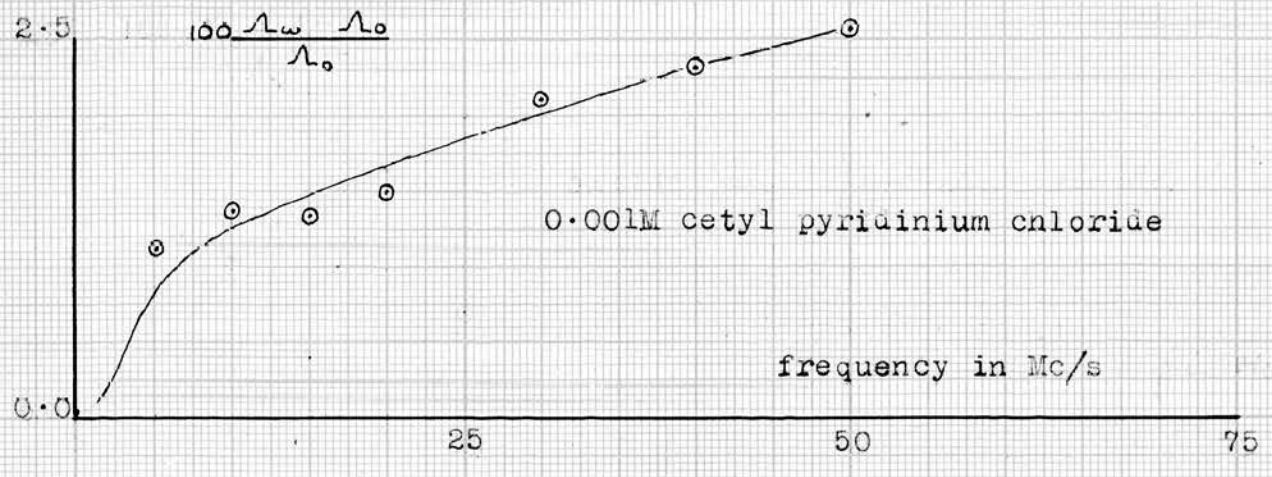
figures for the required concentrations but at higher temperatures. These, when conductivity is plotted against temperature, give approximate values of conductivity at 25°C. of 78, 63 and 52 mhos. for 0·001, 0·002 and 0·003 M cetyl pyridinium chloride. The first of these results gives better agreement with the present values but the remainder correspond closely to the data of Malsch and Hartley.

By any other available data, the measurements of Schmid and Larsen are high, the most probable cause being any other electrolytic impurity.

Conductivity Results at High Frequencies. Unlike the results of Schmid and Larsen, the present results have been corrected theoretically for the high-frequency effect of potassium chloride. Approximations have been used in calculating the corrections but these have a very small effect on a correction already small. In general, the high frequency effect observed with the colloidal electrolyte solutions is much greater than any of the corrections applied and in consequence these corrections have little influence on the shape of the conductivity dispersion curve.

With reference to the variation of high-frequency effect with frequency as shown in Figs.22-30, it will be observed that in all cases there is a rise in effect with frequency as expected on the basis of the Debye-Falkenhagen theory and as previously found by other

Figs. 28, 29.


2·5
$\frac{100\,\Lambda_\omega\ \Lambda_0}{\Lambda_0}$
0·001M cetyl pyridinium chloride
frequency in Mc/s
0·0
25
50
75

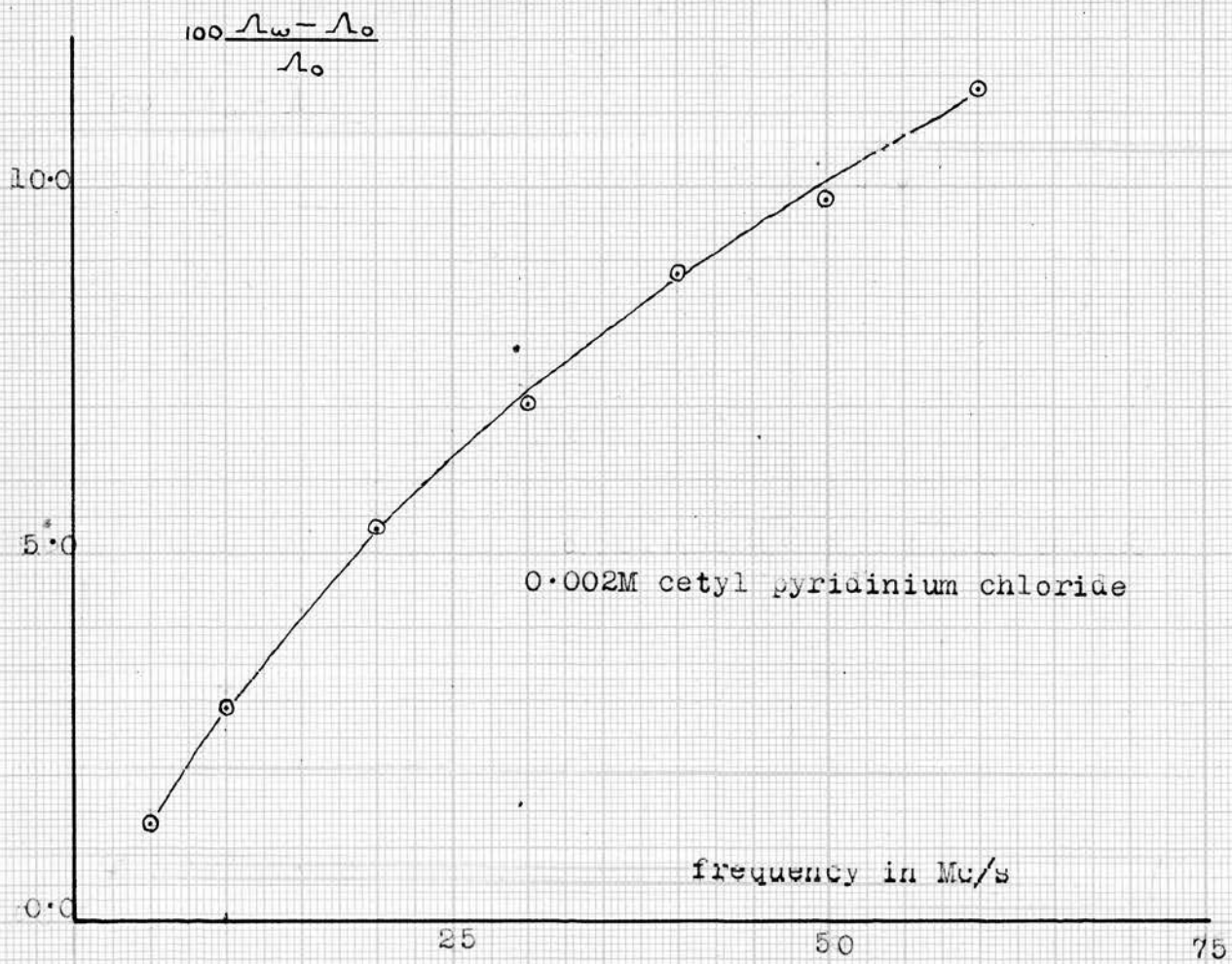
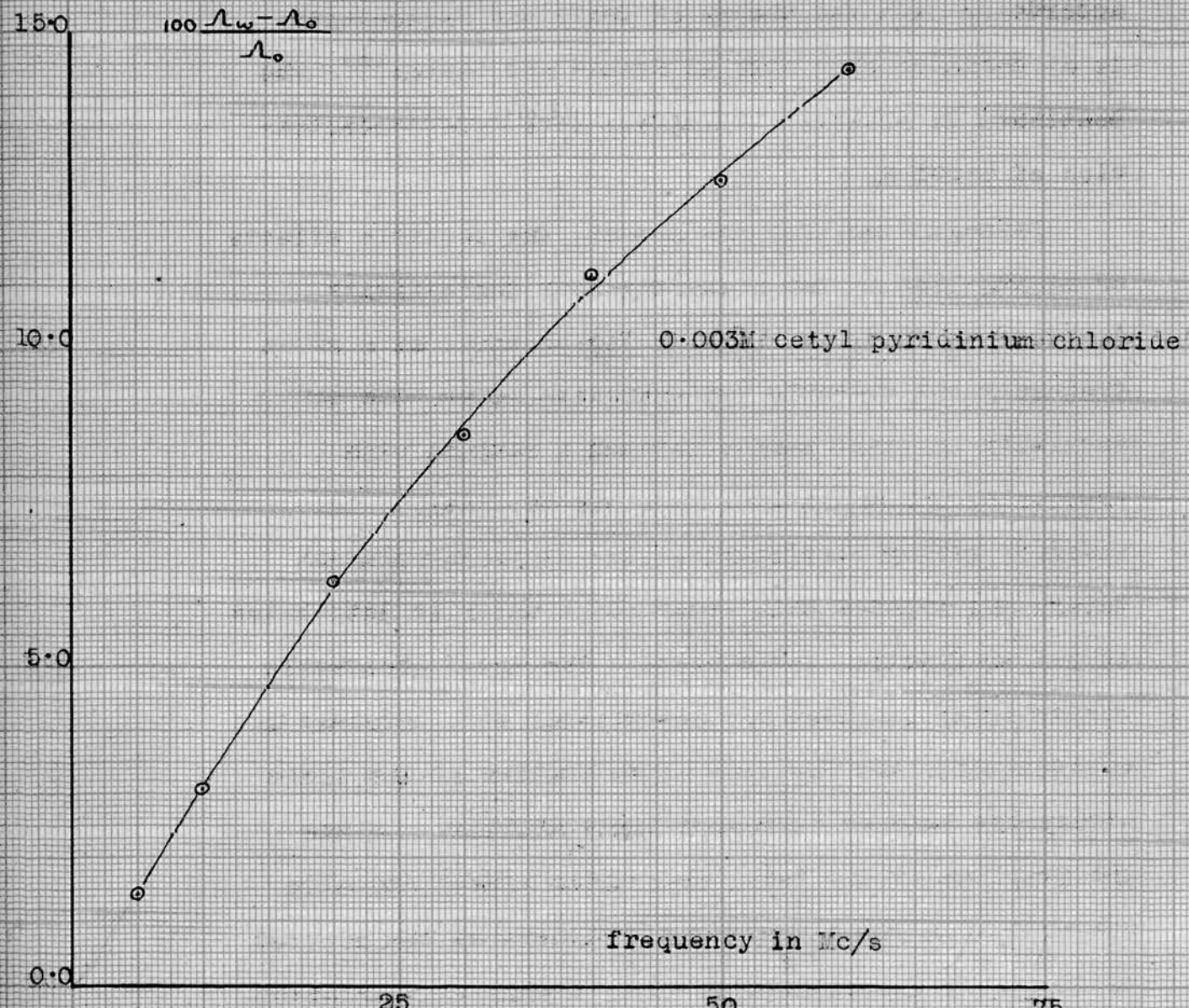

$\frac{100\,\Lambda_\omega - \Lambda_0}{\Lambda_0}$
10·0
5·0
0·002M cetyl pyridinium chloride
frequency in Mc/s
0·0
25
50
75

Fig. 30.


15·0
10·0
5·0
0·0
$100\frac{\Lambda_w - \Lambda_0}{\Lambda_0}$
0·003M cetyl pyridinium chloride
frequency in Mc/s
25
50
75

investigators.[6][8] Except in the case of 0·005 M sodium dodecyl sulphate solution and in that of the smallest concentration of cetyl pyridinium chloride studied (0·001 M), the observed effects are greater than those found in simple strong electrolytes. For sodium dodecyl sulphate, the high-frequency effect falls off in very dilute solution tending to zero at infinite dilution. This behaviour, though in accordance with the theory of Debye and Falkenhagen, is at variance with work of Schmid and Larsen,[6] who continued to observe a 3% effect even at a concentration of 0·003 M.

Disregarding, for the moment, the possible effects of aggregation on the high-frequency conductivity increase we find, as shown in Fig.33 that, at a given frequency and suitable concentration range, the conductivity increase passes through a maximum with increasing concentration. In its application to ordinary strong electrolytes, the Debye-Falkenhagen theory anticipates this observation which it attributes to two conflicting tendencies. The total observable conductivity increase becomes greater with increase in concentration but the time of relaxation of the ionic atmosphere becomes correspondingly shorter. Since the fraction of the total observable effect actually measured at a given frequency increases as the product of frequency and relaxation time, a smaller relaxation

time results in a smaller measured fraction. Over a suitable concentration range, the displacement of the relaxation time can become the dominant factor and cause a decrease in the observed effect at a fixed frequency. This relaxation time displacement is thus responsible for the decrease in the high-frequency effect at the higher concentrations.

A direct test of the applicability of the Debye-Hückel-Falkenhagen theory to the present results is unfortunately difficult, if not impossible. In the first instance, we require to know the mobilities of, and charges on, the ionic aggregates. Furthermore, the aggregation itself may invalidate the application of the theory. Hartley,[9] from a detailed consideration of the effects of aggregation, comes to the conclusion that the theory will predict atmosphere effects which are, in fact, too large. In some cases the concentrations of electrolyte are such as to make it improbable that the theory can be legitimately applied, quite apart from the fact that aggregation leaves the actual concentration of ions involved very uncertain. Consequently, there are too many unknowns for straightforward mathematics to be attempted. There remains the possibility of finding an approximate solution to this problem by means of a graphical method.*

* The writer is indebted to Mr. F. Stern of the Dewar Crystallographic Laboratory for this suggestion.

To be able to achieve fitting of two curves, the writer realised that some common, interchangeable scale had to be employed. Falkenhagen[10] has worked out the values of $\frac{\Lambda_{1\omega}}{\Lambda_{10}}$ where $\Lambda_{1\omega}$ is the contribution to the lowering of equivalent conductivity at frequency ω and Λ_{10} the contribution at zero frequency, for various values of $\omega\theta$ where θ is the relaxation time and $\omega = 2\pi f$, where f is the frequency in cycles per second, and for various values of "q" which is dependent on the mobilities and valencies of the ions involved. For "q" values between 0·5 and 0·3 which Falkenhagen gives, the relationship between $\omega\theta$ and $\frac{\Lambda_{1\omega}}{\Lambda_{10}}$ is not materially altered. A "q" value of 0·5, the value for a uni-univalent electrolyte, was chosen. If the experimental curve is plotted with respect to frequency and Falkenhagen's plotted with respect to $\omega\theta = 2\pi f\,\theta$ on different pieces of logarithmic graph paper, both values on the x-axis, the scales are related by a factor of $2\pi\theta$ which corresponds to a simple horizontal displacement of the two graphs. The experimental value $100(\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o})$ is related to $100(1 - \frac{\Lambda_{1\omega}}{\Lambda_{10}})$, which may be calculated from the data given by Falkenhagen, by the two constants at any specified concentration Λ_{10} and Λ_o . Thus if the logarithms of the experimental and theoretical values are plotted on the linear y-axis of both graphs, multiplication or

Fig. 31.

$\log_{10} 100 \frac{\Lambda_{10} - \Lambda_{1\omega}}{\Lambda_{10}}$

⊙ Experimental points-plotted frequency in Mc/s (log.scale) against $\log_{10} 100 \frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$ (linear scale)

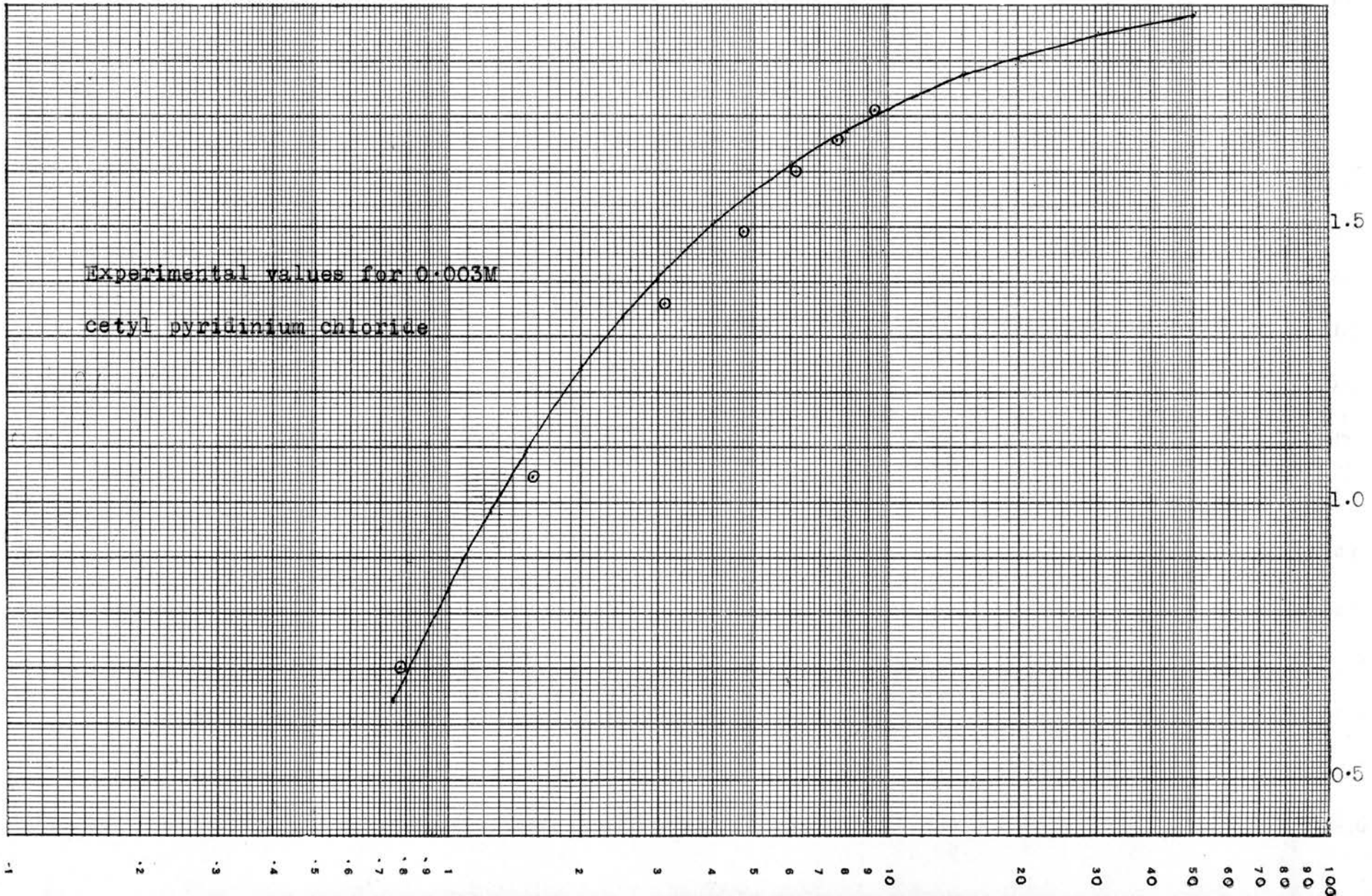
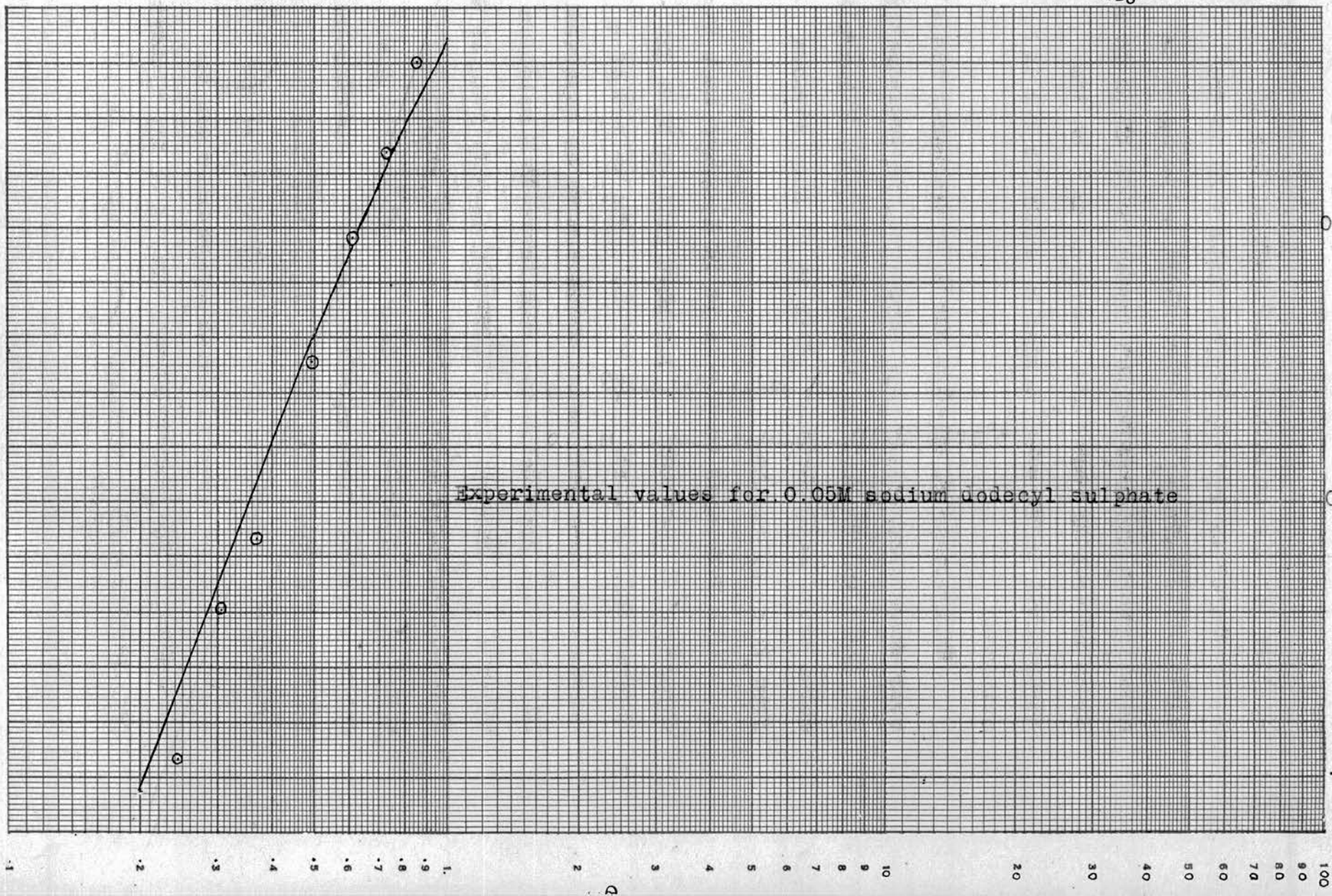


Fig. 32.

$\log_{10} 100\frac{[\Lambda_{10}-\Lambda_{14}]}{\Lambda_{10}}$

⊙ Experimental points-plotted frequency in Mc/s (log.scale) against $\log_{10}\ 100\frac{\Lambda_w - \Lambda_0}{\Lambda_0}$ (linear scale)



division by the constants again corresponds to displacement of the two graphs, this time in the vertical direction. For practical purposes it is advantageous to transfer the experimental graph to a piece of tracing paper and superpose this on the theoretical curve until a good approximate fit is obtained.

Unfortunately, despite the wide frequency range over which experiments were conducted, in practically all cases only a small portion of the total dispersion curve could be explored. This is at once obvious from Figs. 31 and 32.

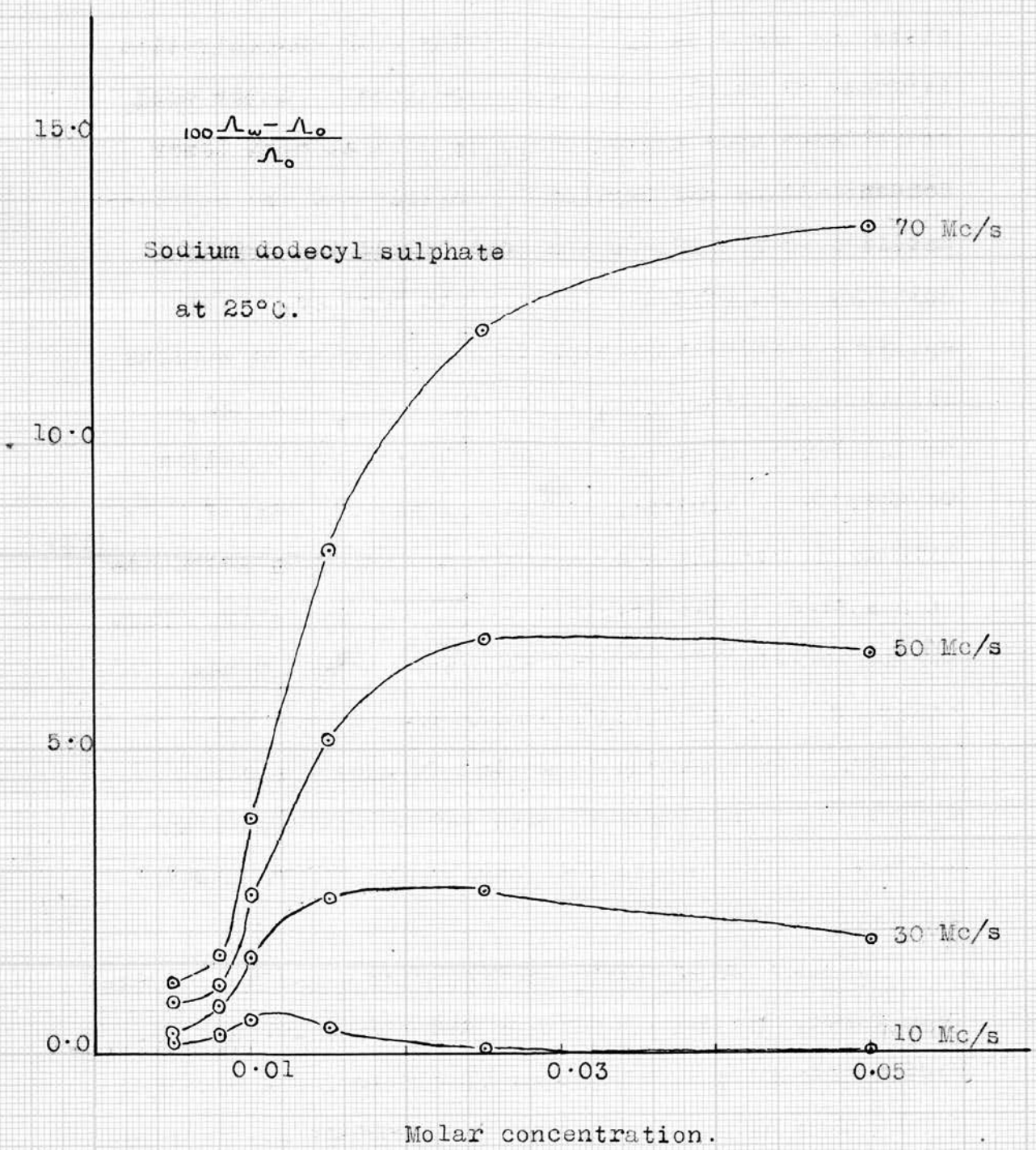
With reference to Fig.31 it is observed that the experimental curvature is somewhat smaller than the theoretical one based on $q = 0.5$. The effect of q values much less than this, which are to be expected if the cetyl pyridinium chloride in 0·003 M solution behaves as a uni-multivalent strong electrolyte, is to flatten the theoretical curve. A much better fit would, in all probability, be obtained by taking a suitable q value into account though the experimental curve would have to be displaced further down the theoretical. Despite this, some estimate of the conductivity at extremely high frequencies can be attempted. The high-frequency effect at the highest frequency employed for this solution (at 60 Mc/s)

corresponds to a $\log_{10} 100 \frac{\Lambda_{10} - \Lambda_{1\omega}}{\Lambda_{10}}$ value of about 1.7, i.e. about 50% total dispersion. At the specified frequency, the high-frequency effect is 14·3%, so that complete dispersion would result in a 28·6% effect. In other words, the conductivity would ultimately rise to at least 128·6% of its low-frequency value.

Turning now to Fig.32, where the high-frequency effect curve for 0·05 M sodium dodecyl sulphate has been superposed on a suitable portion of the same theoretical curve, we observe that a much better fit can be realised. Again this is to be expected on the Debye-Falkenhagen theory since the lower regions of the theoretical dispersion curve are practically independent of the "q" value; calculating in a similar manner to that used above, we find that a 6·3% dispersion gives a high-frequency effect of 13·5%. Complete dispersion must therefore result in a conductivity increase of over 200%, or a conductivity over 300% of the low-frequency value. Such a conductivity, in excess of the infinite dilution conductivity, requires some explanation. As has been mentioned, Hartley[9] predicts that the atmosphere effects will be smaller than anticipated on the Debye-Hückel theory, though the present results indicate that these may still be very appreciable.

As originally pointed out by McBain,[11] a

Fig. 33.


15·0
$100\frac{\Lambda_\omega - \Lambda_o}{\Lambda_o}$
Sodium dodecyl sulphate
at 25°C.
70 Mc/s
10·0
50 Mc/s
5·0
30 Mc/s
10 Mc/s
0·0
0·01
0·03
0·05
Molar concentration.

conductivity increase consequent on aggregation was to be expected on the basis of Stoke's Law if the total charge on the ions was unneutralised. McBain, at that time, considered that this effect was responsible for the rise in conductivity with concentration increase at fairly high concentrations. Later work established that aggregation occurred at much lower concentrations and Hartley[5] attributed the increased (12)
mobility of paraffin-chain ions beyond the critical point to this effect. Malsch and Hartley,[5] by (5)
applying sufficiently high field-strengths to aqueous solutions of cetyl pyridinium chloride, observed a conductivity in excess of that at infinite dilution. In this case, however, the high field may itself produce dissociation of micelle and adhering gegenions (13)
as realised by the original workers. Recently, Kraus and co-workers[14][15] have observed maxima in the equivalent conductivity/concentration curves for colloidal electrolytes dissolved in water-methanol mixtures. These workers have not yet attempted an explanation but the results may be due to the higher mobility of micelles#.

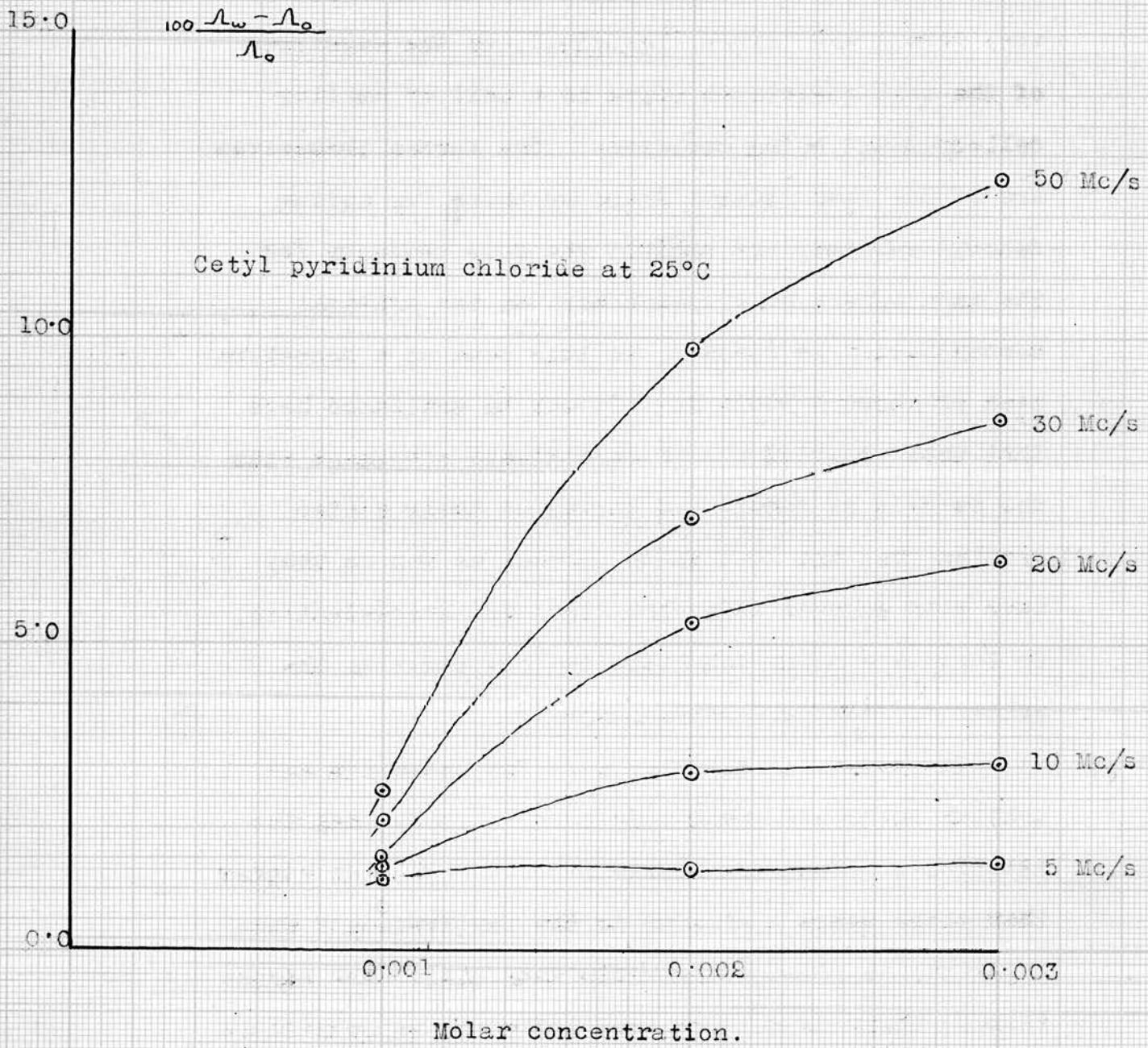
Examination of the high-frequency effect/concentration curve, Fig.33, at various fixed frequencies, for sodium dodecyl sulphate shows that there is a distinct change in slope at the critical concentration. If one

Professor McBain expressed this opinion to the writer.

attributes the large high-frequency effects observed above the critical concentration to interionic action and assumes that the interionic effects arise, in turn, from large, highly-charged micelles of the Hartley type, then the rise in high-frequency effect indicates the formation of these micelles. Since large atmosphere effects are indicated beyond the critical concentration, these may have some bearing on the interesting results of Kraus and co-workers (loc.cit.), the variation in dielectric constant of different water-methanol mixtures suitably modifying the interionic forces. McBain, it may be noted, does not admit the existence of interionic effects of such magnitude and considers instead that the charges on the micelles are so far apart that they behave as though independent.

Below the critical concentration, the high-frequency effect does not appear to diminish to the extent expected if the colloidal electrolyte behaved simply as a uni-univalent electrolyte. Indeed, there may be some incipient micelle formation but the behaviour found is much more in accord with that anticipated for a simple electrolyte than the results of Schmid and Larsen[6] would seem to indicate.

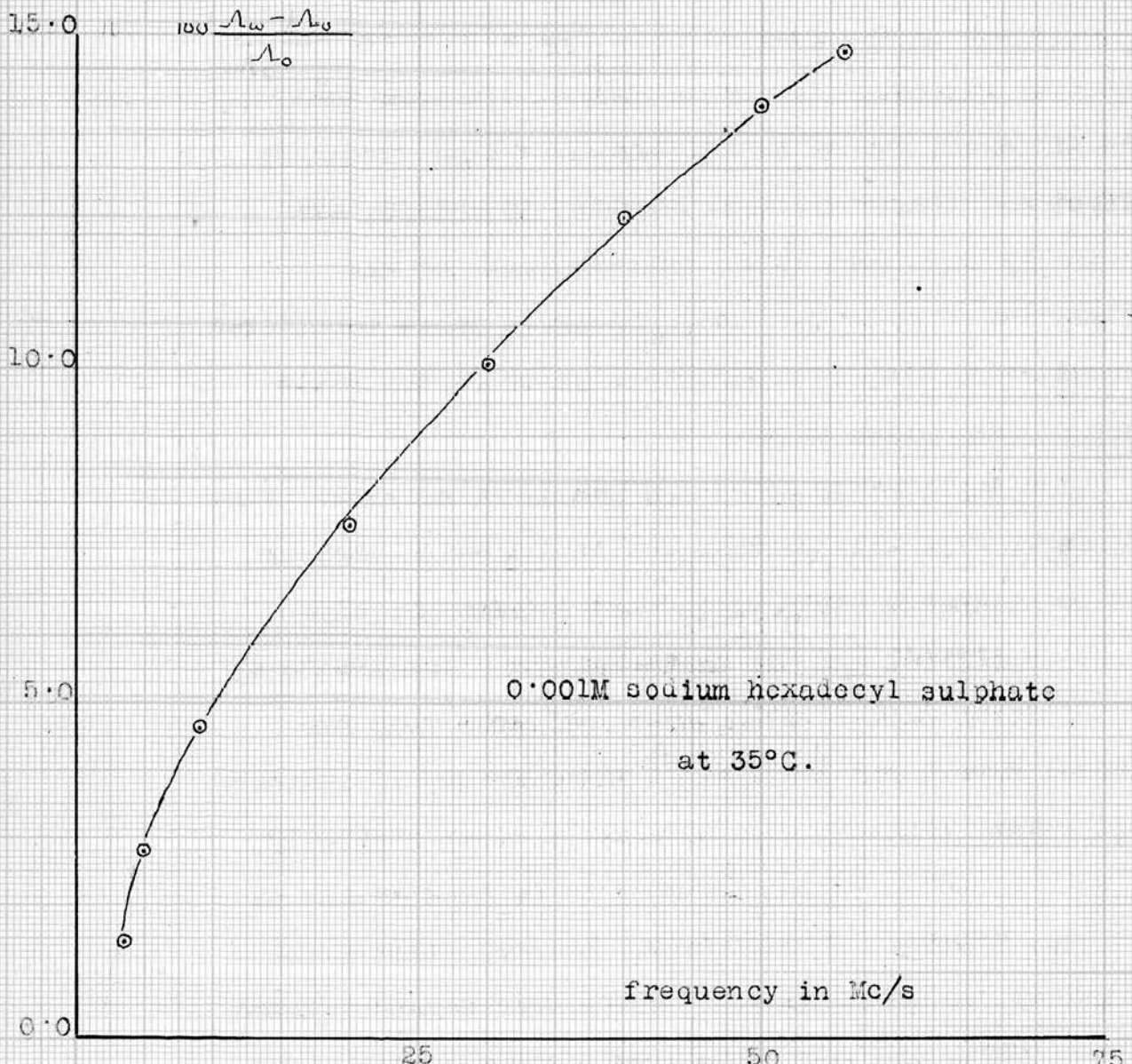
Fig. 34.


15·0
$100\frac{\Lambda_w - \Lambda_o}{\Lambda_o}$
Cetyl pyridinium chloride at 25°C
10·0
5·0
0·0
50 Mc/s
30 Mc/s
20 Mc/s
10 Mc/s
5 Mc/s
0·001
0·002
0·003
Molar concentration.

Turning now to the iso-frequency curves for cetyl pyridinium chloride, Fig.34, it will be seen that measurements were not carried out beyond the critical concentration in this case, as it was considered at the time that no further useful information could be obtained. The writer was not limited, as were Schmid and Larsen (loc.cit.), by the magnitude of the cell resistance owing to a cell of smaller cell-constant being employed. The curves themselves are of the same general shape as those for sodium dodecyl sulphate and exhibit the same tendency for the main effect to approach zero as the critical concentration is reached, in this case at a concentration of about 0·00075 M. It may be mentioned here that these results are in approximate agreement with the results of Schmid and Larsen at their stated wavelengths, and that their curves, as far as they have been pursued below the ciritical concentration, indicate a similar behaviour to that found by the writer for sodium dodecyl sulphate.

The curves of these workers for potassium and calcium salts of arabic acid seem to imply that the interionic effect diminishes at concentrations higher than those where a minimum in the low-frequency conductivity is observed. While they admit some uncertainty, their conclusions may indeed be unjustifiable since Fig.33 indicates that, at a suitably high

Fig. 35.


15·0
10·0
5·0
0·0
$100\frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$
0·001M sodium hexadecyl sulphate
at 35°C.
frequency in Mc/s
25
50
75

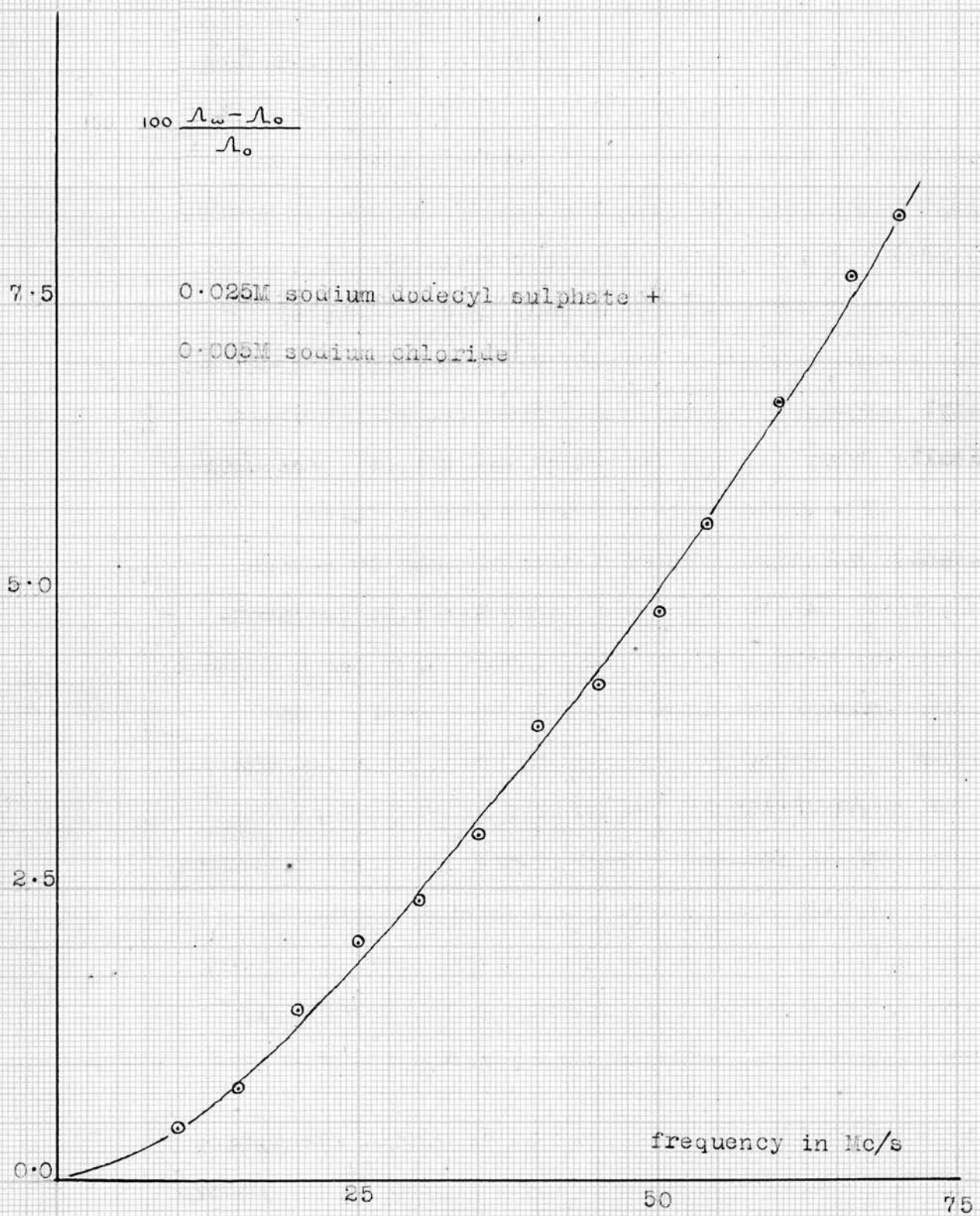
frequency, the rise in the high-frequency effect with increasing concentration, may continue. The shift of relaxation time θ with concentration increase is sufficient to produce a diminution in effect with increasing concentration at a fixed frequency as illustrated by the results at 10, 30 and 50 Mc/s given in Fig.33. It may be pointed out here that the different shapes of the curves of high-frequency effect and frequency, e.g. Figs.26, 30 and 35, are basically explained by the relationships of the relaxation time to the fixed frequency range considered. Essentially, they form different parts of the basic type of dispersion curve.

The experiments on sodium hexadecyl sulphate, Fig. 35, were originally carried out to determine whether any relationship could be deduced between the high-frequency effect and the chain-length. Low-frequency conductivity data at 30°C. were available from the work of Howell and Robinson[2] which seemed to indicate that sodium hexadecyl sulphate would be sufficiently soluble at 25°C. for experiments to be carried out at this temperature. It was found, however, that these solutions, at least above 0·001 M, were supersaturated. Only at 35°C. did they become sufficiently stable for determinations to be made. While no direct comparison with the sodium dodecyl sulphate results was possible,

these results, together with those for cetyl pyridinium chloride, indicated that a large high-frequency effect was not so much dependent on the value of the concentration as on whether this concentration lay above or below the critical.

The "Salt Effect." Reference must now be made to the results shown in Fig.36 for a solution containing 0·025 M sodium dodecyl sulphate and 0·005 M sodium chloride. Comparison with the curve for 0·0025 M sodium dodecyl sulphate alone, Fig.26, at first seems to indicate that addition of simple electrolyte diminishes the high-frequency effect. It must be remembered, however, that the results given in Table VIII, p.95 are based ultimately on the low-frequency conductivity of the mixture. If we reckon the high-frequency effect, on the conductivity of the sodium dodecyl sulphate itself, there is, if anything, an increase in effect with addition of sodium chloride. It has been pointed out that the substantial high-frequency effect above the critical concentration can be explained by increasing formation of micelle and hence we should infer that the sodium chloride aided micelle formation. Quite apart from other effects, the salt would be expected to shorten the relaxation time of the mixture and hence reduce the high-frequency effect at a given frequency.

Fig. 36.


$100\,\frac{\Lambda_\omega - \Lambda_0}{\Lambda_0}$
7·5
5·0
2·5
0·0
0·025M sodium dodecyl sulphate +
0·005M sodium chloride
frequency in Mc/s
25
50
75

An increase in micelle formation on the addition of a simple electrolyte has been stated by McBain and Searles[16] to explain a conductivity, greater than would be anticipated from the sum of the two components, by adding hydrochloric acid at various concentrations to solutions of undecylsulphonic acid. Hartley[17] also considered that addition of potassium chloride to cetyl pyridinium chloride solution caused increased micelle formation and decreased the critical concentration. The writer made a 0·005 M sodium dodecul sulphate solution 0·0025 M with respect to sodium chloride. At 70 Mc/s, the corrected high frequency effect was 0·3% less for the mixture than for a 0·005 M sodium dodecyl sulphate solution by itself. An estimate allowing for the result being based on the total conductivity of the mixture might indicate a higher result for the sodium dodecyl sulphate component in the mixture than for the colloidal electrolyte alone but the magnitude of the experimental error and change in relaxation time for the mixture, make any deductions from this experiment uncertain.

Dipole Absorption. The question of dipole absorption which was considered by Schmid and Larsen[6] to explain a 3% apparent high-frequency effect for sodium dodecyl sulphate at concentrations below the critical, must now be explored. Large dipole effects exist in

amino acids and protein solutions and the analogy between proteins and the colloidal electrolytes with which we are dealing at present has often been emphasised. Kirkwood[18] points out that amino acids and proteins exist in solutions partly as neutral molecules and partly as positive and negative ions. At the isoelectric point the neutral molecules predominate and while leaving no net charge, possess a high dipole moment.

At low frequencies, the high dielectric constant of a protein solution can be attributed mainly to the orientation of its constituent dipoles. When, however, the applied frequency is raised, frictional forces overcome the orienting torque. The dipoles no longer follow the field and a decrease in dielectric constant is observed.[19] In the region where there is incomplete orientation of the dipoles, there is a phase-displacement between the position of the dipole and the polarity of the applied field. An in-phase component of the displacement current causes ohmic loss in the solution which behaves as an increase in conductivity, reducing the observed high-frequency deflection in an identical manner. Furthermore, calculations of the critical frequency, for a large spherical particle of radius the order of the length of the paraffin chain[20][21] reveals that this critical frequency lies in the frequency range in which the

present experiments were conducted. There is little possibility of such a large degree of micelle formation below the critical concentration as would be necessary to explain Schmid and Larsen's observed effect. On the other hand, they consider the effect to arise from the dodecyl sulphate ion itself but probably the frequencies employed are for too low for the results to be so attributed.

When it was found that the high-frequency effect for sodium dodecyl sulphate at concentrations above the critical did not attain the values found by Schmid and Larsen at their stated frequencies, the existence of the 3% effect below the critical concentration was immediately doubted. Further experiments, conducted at much higher frequencies produced results, for concentrations above the critical concentration, comparable with their previous work. It was therefore thought probable that, despite the failure to reproduce their values at their stated frequencies, these results could be duplicated at higher frequencies. Accordingly, the information for 0·005 and 0·008 M sodium dodecyl sulphate was extended to the highest frequencies available. No 3% effect was obtained in spite of the addition of the potassium chloride correction. The writer was therefore forced to the conclusion that whatever the cause of the previous results, the effect itself did not exist.

It is to be noted that, for cetyl pyridinium chloride at suitable frequencies where the results roughly correspond to those of the writer, the values are already well below 1% at concentrations above the accepted critical concentration.

The Investigation of Schmid and Larsen.[6] Some explanation of the large discrepancies between the results of the present investigation and of the previous work of Schmid and Larsen must be attempted. These discrepancies may be summarised as follows:

(1) For sodium dodecyl sulphate there is no 3% effect below the critical concentration.

(2) Above the critical concentration the results for sodium dodecyl sulphate are inconsistent with the present information at the frequencies stated.

(3) A sufficiently large error in frequency calibration is practically ruled out by essential agreement for the cetyl pyridinium chloride results.

In the apparatus originally used,[22] the high-frequency conductivity cell was connected, via isolating capacitors, across the tuned circuit in which the high-frequency currents are oscillating and whose constants principally determine the frequency of oscillation. When, however, this tuned circuit is very heavily damped by the resistance of the conductivity cell and by other losses associated with it, oscillation in the

tuned circuit becomes more and more difficult.

In addition to the obvious tuned circuit, other unintentional components are present. These mainly consist of the inter-electrode capacitances of the values, the capacitances between connecting leads and the inductance of these leads. When oscillation becomes difficult in the main tuned circuit, high-frequency oscillations may arise in these subsidiary components, practically independent of the original frequency-determining circuit. Such secondary oscillations are known as "parasitics"[23] and are normally higher in frequency than the original owing to the circuit constants being very much smaller.

For cetyl pyridinium chloride, the concentrations over the required range of measurement are extremely small and all resistance values correspondingly high, so that the tuned circuit can fulfil its intended purpose. Results, therefore, agree in order of magnitude with those of the writer. The sodium dodecyl sulphate solutions are much higher in concentration and cell resistances very much lower, so that it is probable that parasitic oscillations arise and the high-frequency effect is determined at these parasitic frequencies. In fact, similar results to those found by Schmid and Larsen can be obtained at suitably high frequencies.

If this is the correct explanation, then a range

of cell resistances ought to exist where the circuit changes from one oscillation mode to the other or where it is somewhat unstable in either mode. Such a range may coincide with the sodium dodecyl sulphate solutions below the critical concentration and account for the discrepancies found by the writer in this region, e.g. Schmid and Larsen claim a 3% effect at 12 metres, the writer's result being 0·3%.

Naturally, since reinvestigation of other results obtained by Schmid and co-workers[6][8][22] has not been carried out, the validity of these results at the frequencies stated has not been checked.

Summary.

(1) Apparatus for the determination of high- and low-frequency conductivity has been devised and constructed.

(2) The difficulties of temperature control in high-frequency conductivity investigations have been overcome by a new form of electronic proportioning regulator.

(3) Measurements of the low-frequency conductivity of aqueous solutions of sodium dodecyl sulphate at 25°C. have been carried out over a wide range of concentration.

(4) Measurements of the high-frequency conductivities of aqueous solutions of sodium dodecyl sulphate and cetyl pyridinium chloride at various concentrations at 25°C. and of sodium hexadecyl sulphate at one concentration at 35°C. have been made up to frequencies of 70 Mc/s.

(5) In all cases an increase of high-frequency effect with frequency has been observed. Evidence for the effect being attributable to the ionic atmosphere has been discussed.

(6) For sodium dodecyl sulphate, at and below the critical concentration, no evidence of the dipole absorption effect claimed by Schmid and Larsen has been found. The effect observed at these concentrations indicates substantial agreement with the view that sodium dodecyl sulphate exists there mainly as a uni-

univalent electrolyte.

(7) Approximate agreement with the Debye-Falkenhagen theory has allowed estimates of conductivity at very high frequencies to be made.

(8) A possible rise at sufficiently high frequencies of the conductivity for 0·05 M sodium dodecyl sulphate to values above the infinite dilution value has been discussed.

(9) Investigation of the "salt-effect" has indicated that small additions of simple electrolyte may slightly increase the observed high-frequency effect.

(10) An explanation of the discrepancies between the present work and that of Schmid and Larsen has been advanced.

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FIG. 37

SODIUM DODECYL SULPHATE AT 25°C.

o OWN VALUES

Δ THOSE OF HAFFNER, PICCIONE AND ROSENBLUM.